THE COMPOSITION AND ASSAYING OF MINERALS

Barytes, or Heavy Spar [*Frontispiece*

THE COMPOSITION AND ASSAYING OF MINERALS

by

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and

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PREFACE

THIS book is not intended to be a complete guide to mineralogy, and although the crystalline forms of numerous metallic minerals are referred to in the descriptions of the ores mentioned, no attempt has been made to illustrate the various systems which occur in crystallography and usually accompany a book on this subject; nor are methods described for the determination of the physical characteristics of minerals, such as the angles between the faces of crystals, hardness or density, which always form a part of books on pure mineralogy. On the contrary, the book relates primarily to the chemical composition of minerals, with the object of providing a handy guide to their qualitative and quantitative examination that is suitable for use by mineralogists, metallurgists, geologists, chemists in mine laboratories, and students in schools, technical colleges, and universities. Advanced methods of examination, such as the use of the spectrograph, have not been included, since expensive apparatus is not usually available in the laboratories for which the book is intended, whilst recently developed spot tests for inorganic radicals, using organic reagents, have also not been included, since such methods are more suitable for determining trace elements rather than the gross proportions of bases and acids present in minerals.

The quantitative assay methods originally formed part of a small book by one of us, which was published in 1940 It has been pointed out since, by several geological chemists, that the original book would be much more valuable and useful to its readers if descriptions of the chief minerals were also given, together with qualitative tests for the commoner radicals. For these reasons the present book has been produced, and, it is hoped, may be found useful to all those interested in geology and the composition of minerals.

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PART I

QUALITATIVE EXAMINATION

THE IDENTIFICATION OF BASES AND ACIDS

THIS book is not a complete guide to practical geology, nor does it deal in detail with the structure of minerals, but it is essentially a laboratory text-book, giving methods for the identification and assay of ores and minerals, with some physical properties of many common minerals. Assay methods for ores may be divided into two classes: (1) dry assays, employing the use of fluxes, and (2) wet assays, usually called analyses. In this book wet assaying, or analytical procedure, is generally described.

Before an assay can be carried out, however, it is necessary to identify the mineral, or to determine the nature of the basic and acidic radicals that are present if the identity of the mineral is unknown. This identification is possible from the results of the qualitative tests commonly used for the identification of inorganic compounds, which are described below.

PRELIMINARY TESTS FOR RADICALS

The following tests are generally used for the examination of unidentified minerals before the assay proper is carried out:

A. *Decomposition by Heat*

The substance is heated over a bunsen burner in a small tube sealed at one end and made out of hard glass. The heat must be applied very gently at first, being increased gradually to red heat. This treatment ascertains whether the substance is completely or only partly volatile, or whether any colour change takes place. The following effects will be observed and the appropriate deductions made:

1. Water is given off in a state of vapour, which condenses in the cold part of the tube. This indicates water of crystallization, or hydration, or water mechanically held in the substance.
2. Gas or vapour is evolved, such as oxygen, oxides of nitrogen, or sulphur dioxide. Oxygen, which may be identified by relighting

E. *Qualitative Separation of Metals in a Mineral*

As a result of the above tests, some knowledge of the composition of an unknown mineral will have been obtained. It is then necessary to determine exactly what basic and acidic radicals are present. In order to do this, and before carrying out a quantitative analysis, it is necessary to obtain a representative sample of the mineral, to prepare this for analysis, and to render all constituents soluble in dilute acids.

Preparation of Sample. A representative sample of the ore, of several pounds weight, should first be obtained, wrapped in strong brown paper, placed on a smooth iron plate and reduced to small pieces and coarse powder by means of hammer blows. This is preferred to the use of mechanical grinding equipment, with the risk of contamination by abraded metal or previous samples. The sample is then well mixed into a uniform circular heap, quartered, and opposite quarters taken. The residue is remixed and the procedure repeated until only a few ounces remain. This is then ground in an agate mortar until all passes a 120-mesh B.S. sieve or its equivalent. Reduction to a fine powder is essential to render most minerals readily soluble in acids or fusion mixtures. The prepared sample should be preserved in a clean, dry, wide-mouth, glass-stoppered bottle.

Preparation of Solution. Few minerals are soluble in water, but all must be dissolved before analysis is possible. It is desirable to achieve solution by the simplest method possible, so that mild reagents are used first, and stronger reagents, or more powerful techniques, are used only if the simpler methods fail.

Samples should first be treated with dilute hydrochloric acid and heated gently. Carbonates, such as magnesite and chalk, will effervesce vigorously, giving off carbon dioxide. Should hydrochloric acid alone produce little or no result, then nitric acid or aqua regia (nitric and hydrochloric acid, HNO_3+3HCL) should be used to effect solution. This is especially necessary with carbonates of copper and lead. On the addition of hydrochloric acid to metallic sulphides, sulphuretted hydrogen is liberated.

The majority of the mineral oxides are soluble in acid solutions, such as hydrochloric acid and nitric acid, if sufficient time is given for the digestion. There are some mineral oxides, however, which do not dissolve readily in acids; for example, chromite, quartz, rutile and cassiterite. These require special fusion methods. Some silicates, when very finely powdered, may be decomposed on being treated with boiling hydrochloric acid, to form a gelatinous precipitate, which settles down as a fine deposit. In most cases, however, silicates are unaffected by acids and require treatment by fusion mixture, followed by hydrochloric acid, in order to get the various bases present into solution. Examples of minerals requiring treatment with fusion mixture are barytes, celestine and anglesite, sulphate of barium, strontium and lead, as well as several phosphatic minerals. The treatment of such minerals is carried out as follows:

1·5 gram of the prepared sample is carefully weighed out into a fairly large platinum crucible, to which is added about six times its weight (9–10 gram) of fusion mixture, consisting of sodium carbonate and potassium carbonate in equal proportions by weight. The powders are then mixed in the crucible with a smooth glass rod and it is best, after mixing, to turn out the contents on to a piece of black glazed paper, and, when fusing, to add the mixture little by little, since considerable frothing occurs. When all frothing has ceased, remove the crucible from the bunsen flame; place in a red-hot muffle and continue heating until the mass is clear and tranquil; then remove from the muffle. The time in the muffle at a bright red heat should be about 15 minutes. Allow the crucible to cool to just below redness, then place on an iron plate, or in a basin of cold water, in order to crack the mass from the crucible. Place in an evaporating basin and add about 100 ml. distilled water, and boil for about 30 minutes. Add dilute hydrochloric acid gradually, keeping the dish or beaker covered with a clock glass and agitating gently after each addition of acid. When all effervescence has ceased, and the crucible is free from adhering matter, take the crucible and lid carefully out and rinse, adding the rinsings to the liquid in the dish or beaker. The solution should then be ready for analysis. During the analysis of an insoluble silicate there must be no gritty lumps in the gelatinous precipitate produced. If there are any lumps the fusion will have been incomplete. This may be due to the sample having been too coarse in the first instance, or to not having used sufficient fusion mixture, or to imperfect mixing.

Identification of Metals. Evaporate the solution to dryness, finishing the evaporation on a sand bath or in an air oven at 150° C. Cool, digest in hot dilute hydrochloric acid and filter. Wash the residue into a beaker and add hot dilute nitric acid, when all but the silica should dissolve. Combine the filtrates and test for the metals present by following the general scheme for the qualitative analysis of metals given facing page 128. The same procedure should be followed with dilute acid solutions of minerals or inorganic compounds that are obtained without the use of fusion mixture.

Identification of Acid Radicals. Carbonates are identified by the evolution of carbon dioxide on warming with dilute hydrochloric acid, as described previously. *Chlorides* are identified by the formation of a white curdy precipitate on the addition of silver nitrate to a dilute

Borax Bead

Substance	*Oxidizing Flame*		*Reducing Flame*	
	Hot	Cold	Hot	Cold
Silica	Colourless	Colourless	Colourless	Colourless
Alumina	”	”	”	”
Tin oxide	”	”	”	”
Silver oxide	”	”	Grey or colourless	Grey or colourless
Baryta	”	”	”	Colourless or opaque
Strontia	”	”	”	”
Calcium oxide	”	”	”	”
Magnesia	”	”	”	”
Titanium (TiO_2)	Colourless to yellow	”	Yellow to brown	Yellow to brown
Tungsten trioxide	”	Colourless or white	Yellow	Yellowish-brown
Zinc oxide	Yellow	White	Greyish	Greyish to colourless
Cadmium oxide	Reddish-yellow	”	”	Greyish
Antimony oxide	Yellowish	”	Greyish or colourless	Greyish or colourless
Bismuth oxide	Yellow	Yellowish to colourless	Grey to colourless	Grey to colourless
Lead oxide	”	Colourless to opaque	”	”
Molybdenum trioxide	Yellow to red	Colourless	Brown	Opaque brown
Chromium oxide	”	Grass-green	Green	Emerald green
Nickel oxide	Violet	Reddish-brown	Grey to colourless	Grey to colourless
Cobalt oxide	Blue	Blue	Blue	Blue
Copper oxide	Green	Bluish-green	Colourless	Brownish-red
Manganese oxide	Violet or black	Violet or black	”	Colourless
Iron oxide	Yellow to red	Yellow to colourless	Green	Dark green
Cerium oxide	”	Colourless	Colourless	Colourless to porcelain white
Uranium oxide	”	Colourless to yellow	Green	Bottle green or black

Microcosmic salt, $Na(NH_4)HPO_4.4H_2O$

Substance	Oxidizing Flame		Reducing Flame	
	Hot	Cold	Hot	Cold
Silica	Colourless	Colourless	Colourless	Colourless
Alumina	"	"	"	"
Tin oxide	"	"	"	"
Baryta	"	"	"	"
Strontia	"	"	"	"
Calcium oxide	"	"	"	"
Magnesia	"	"	"	"
Titanium (TiO_2)	"	"	Yellow	Violet
Tungsten trioxide	"	"	Dirty green	Bluish
Zinc oxide	Yellowish	White	Grey	Grey
Cadmium oxide	"	"	"	Colourless
Antimony oxide	Colourless to slight yellow	"	"	Grey
Bismuth oxide	Colourless	Colourless	Greyish	Greyish
Lead oxide	"	White	"	"
Molybdenum trioxide	Green	Faint green	Dirty green	Green
Chromium oxide	Reddish-green	Emerald-green	Reddish	"
Nickel oxide	Reddish to brownish-red	Yellow to reddish-yellow	"	Yellow
Cobalt oxide	Blue	Blue	Blue	Blue
Copper oxide	Green	"	Dark green	Brownish-red
Manganese oxide	Violet	Violet	Colourless	Colourless
Iron oxide	Yellow to red	Colourless to yellow	Yellow to red	Colourless to brownish
Cerium oxide	"	Colourless	Colourless	Colourless
Uranium oxide	Yellow	Yellowish-green	Dirty green	Green

solution of the mineral, or a portion of the mineral, in nitric acid. *Silicates* are identified by insolubility in hot dilute hydrochloric acid or nitric acid after rendering the mineral soluble by treatment with acids or fusion mixture in the manner described above. *Sulphates* are identified by the formation of a dense white precipitate on the addition of barium chloride to a solution in hydrochloric acid. This precipitate should be insoluble in boiling nitric acid and also in a solution of ammonium acetate. *Chromates* are indicated by the formation of a yellow precipitate of lead chromate on the addition of acetic acid and lead acetate to a neutral solution. Chromium is also separated and identified in group IV of the general scheme for the qualitative analysis of the metals. *Phosphates* are shown by the formation of a yellow precipitate on the addition of ammonium molybdate to a solution in dilute nitric acid. *Sulphides* are identified by the evolution of hydrogen sulphide when the mineral is treated with hydrochloric acid. *Fluorides* are shown by the etching on the side of the test-tube when the mineral is heated gently with concentrated sulphuric acid. Alternatively, calcium fluoride, prepared by the addition of calcium chloride to an ammoniacal solution of a fluoride and filtering off the solution, may be used for the test. *Nitrates* are shown by the evolution of brown fumes of nitrogen peroxide on warming with concentrated sulphuric acid. During these tests for fluoride and nitrate, hydrochloric acid will be evolved from any chloride present. This should be confirmed by the silver nitrate test described above.

PHYSICAL TESTS

Simple physical tests often serve to identify minerals, particularly when used in conjunction with chemical or geological data. The two most commonly applied physical tests are hardness and specific gravity. The following tables show typical values for these variables over the whole range of naturally occurring minerals:

Hardness

Mineral	*Approximate Degree of Hardness*	*Chemical Name*	*Scale of Hardness*
Talc	can be scratched by the finger-nail	Magnesium silicate	1
Gypsum		Calcium sulphate	2
Calcspar	can be scratched by knife or file	Calcium carbonate	3
Fluorspar		Calcium fluoride	4
Apatite		Calcium phosphate	5
Felspar		Potassium and aluminium silicate	6

Mineral	*Approximate Degree of Hardness*	*Chemical Name*	*Scale of Hardness*
Quartz (rock crystal)	cannot be scratched by knife or file	Silica	7
Topaz		Aluminium fluosilicate	8
Corundum		Crystallized alumina	9
Diamond		Crystallized carbon	10

Specific Gravity

Mineral	*Sp. Gr.*	*Mineral*	*Sp. Gr.*
Platinum	22·07	Marble	3·80
Gold	19·35	Diamond	3·50
Lead	11·35	Aluminium	2·68
Silver	10·50	Rock Crystal	2·65
Copper	8·90	Gypsum	2·3
Iron	7·80	Salt	2·13
Barytes	4·43	Ice	0·93

PART II

METALLIC MINERALS

PROPERTIES AND METHODS OF ASSAY

SILVER, Ag (*Argentum*); atomic weight 107·88

SILVER is a monovalent element, and is a metal of good malleability and high ductility. In this respect silver ranks second to gold, for it can be rolled into thin sheets and drawn out to very fine, thin wire. Metallic silver is a lustrous white metal, specific gravity 10·5, and fuses at 962° C., boiling point 1960° C. Hardness 2·5–3·0.

Silver dissolves easily in nitric acid and also in hot concentrated sulphuric acid, when sulphur dioxide is evolved. The chief minerals of silver are the following:

Native Silver, most frequently found in the form of octahedra. Colour, silver-white, metallic lustre. Hardness 2·5–3·0; specific gravity 10·1–11·1. Frequently found in conjunction with copper and lead, and in much smaller amounts with zinc, antimony, bismuth, mercury and gold ores. Is easily dissolved by nitric acid. Chiefly found in eruptive and sedimentary rock formations in the form of strings or veins.

Argentite or *Silver Glance*, Ag_2S, an important ore of silver found in Mexico and Nevada. Colour lead-grey to black, lustre metallic. Hardness 2–2·5; specific gravity 7·19–7·36; a silver sulphide. Composition: silver 87·1 per cent and sulphur 12·9 per cent. Soluble in nitric acid. The finely powdered mineral when heated in an open tube gives off fumes of sulphur dioxide. When heated on charcoal in the oxidizing flame it gives off fumes, and a bead of metallic silver is formed.

Stephanite, $5Ag_2S.Sb_2S_3$, crystalline form rhombic, usually found as modified rhombic prisms, colour black, lustre metallic. Hardness 2–2·5; specific gravity 6·26. A sulphide of silver and antimony; silver 68·5 per cent, antimony 15·3 per cent and sulphur 16·2 per cent. The finely powdered mineral heated in a tube fuses and forms a sublimate of antimony sulphide, but requires heating for some time before sublimation takes place. The powdered ore, when heated on charcoal, fuses to a dark metallic mass, and forms an incrustation of antimonious acid, H_3SbO_3.

Ruby Silver or *Red Silver* is found in two varieties; (*a*) a dark red ore pyrargyrite, and (*b*) a light red ore called proustite. *Pyrargyrite*, $3Ag_2S.Sb_2S_3$, is dark red to black in colour. Hardness 2–2·5; specific gravity 5·7–5·9. Lustre metallic, fracture conchoidal. *Proustite*, $3Ag_2S.As_2S_3$, is light red in colour, being found in both the granular and massive states, fracture uneven or conchoidal. Hardness 2–2·5; specific gravity 5·4–5·56. Heated in an open tube gives a sublimate of arsenic. The composition of pyrargyrite is approximately silver 59·8 per cent, antimony 22·5 per cent and sulphur 17·7 per cent, and that of proustite: silver 65·4 per cent, arsenic 15·2 per cent and sulphur 19·4 per cent.

Freieslebenite, $5(Ag_2Pb)S.2Sb_2S_3$, a complex ore of silver, lead and antimony. Usually contains about 22–24 per cent of silver. Colour light grey, and also found dark lead-grey. This mineral has a brittle and uneven fracture. Hardness 2–2·5; specific gravity 6–6·4. Frequently associated with galena, PbS, and spathic iron ore; ferrous carbonate, $FeCO_3$.

Polybasite, $(Ag_2SCu_2S)_9.(Sb_2S_3.As_2S_3)$, a complex ore consisting of sulphides of silver, copper, antimony and arsenic, chiefly found in Mexico, Chile and California.

Horn Silver, silver chloride, $AgCl$, found as massive wax-like formations. Colour usually light grey, sometimes greenish-grey or bluish-grey; and on exposure to the air turns a brownish shade. Lustre resinous. Hardness 1–1·5, can be cut like wax; specific gravity 5·5. Composition: silver 75·3 per cent, chlorine 24·7 per cent. Insoluble in nitric acid but soluble in ammonia, and when heated on charcoal yields a globule of silver. Very abundant in South America. Finely ground ore—that is a sample reduced to fine powder in an agate mortar, and then heated on charcoal—gives a malleable bead on reduction.

Qualitative Tests

Salt used: silver nitrate, $AgNO_3$.

1. On the addition of hydrochloric acid a white curdy precipitate of silver chloride forms; insoluble in nitric acid and water, but soluble in ammonia:

$$AgNO_3 + HCl = AgCl + HNO_3$$

In the case of a compound containing minute amounts of silver, only a white opalescence may at first be produced, but if the beaker or tube be kept for some time under warm conditions and shaded from direct daylight, the silver chloride will collect at the bottom of the containing vessel. When exposed to light, silver chloride changes to violet, finally becoming black. Fused with sodium carbonate on charcoal, silver chloride is reduced to metallic silver.

2. Hydrogen sulphide, H_2S, gives a black precipitate of silver sulphide, soluble in boiling dilute nitric acid, and potassium cyanide solution:

$$2AgNO_3+H_2S=Ag_2S+2HNO_3$$

3. Ammonium sulphide, $(NH_4)_2S$, gives a similar black precipitate to that produced by hydrogen sulphide; soluble in boiling dilute nitric acid.
4. Potassium chromate, K_2CrO_4, gives in fairly dilute solutions a brownish-red precipitate of silver chromate; soluble in nitric and sulphuric acids and ammonia solution:

$$2AgNO_3+K_2CrO_4=Ag_2CrO_4+2KNO_3$$

5. Potassium and sodium hydroxides form a precipitate of silver oxide, Ag_2O, as a brownish-grey powder; soluble in ammonia:

$$2AgNO_3+2KOH=Ag_2O+2KNO_3+H_2O$$

6. In the blowpipe reducing flame a borax bead containing a silver compound becomes grey or brownish-grey due to the formation of silver oxide, Ag_2O, which dissolves readily in nitric acid; when heating is continued for some time a bead of metallic silver will finally result.

Quantitative Assays

Silver is normally found associated with galena and zinc-blende, and is in too small a quantity to obtain a satisfactory figure by ordinary wet assay methods, so that a dry assay is used as described in Part III. For the assay of coinage the following method is preferable. A piece of the coin is cut off, weighed accurately and dissolved in dilute HNO_3. The tin is precipitated as metastannic acid and is filtered off, ignited and weighed as SnO_2. If copper is present, the silver is precipitated with HCl or sodium chloride, the former preferred, filtered through a weighed, sintered glass crucible, grade G.3., dried in the steam oven and weighed as AgCl; 1 gram AgCl contains 0·7526 gram Ag.

Where copper is absent, the filtrate from the Sn is made up to 500 ml. in a measuring flask, well shaken, and 50 ml. pipetted into a 500-ml. conical flask. About 10 ml. HNO_3 is now added, together with about 5 ml. saturated iron-alum solution, and the solution titrated with

N/10 ammonium or potassium-thiocyanate solution, a blood-red coloration being formed with an excess of the precipitant.

A very satisfactory method for the estimation of silver in the presence of halides or cyanides is as follows:

A quantity of material containing 0·05–0·09 gram of silver is dissolved in 5·9 ml. of cyanide solution in a litre squat beaker. 50 ml. 10-per-cent sodium-chloride solution is added and decinormal iodine solution run in from a burette until the separation of silver iodide causes a faint opalescence. This is the starting-point for the silver determination, and with care is definable to one drop of iodine. If the point is overrun it may be readjusted by the addition of a little cyanide, a known quantity being added if cyanide also is to be estimated. The solution is now diluted to 800–900 ml. with cold water, starch paste added, and the titration continued until the blue colour is permanent. The volume of iodine added at this stage determines the silver, since I is equivalent to Ag.

Solutions required:

1. Approximately N/5 KCN, containing about 13 gram of KCN and 5 ml. ammonia per litre.
2. N/10 iodine solution, preferably standardized by this method against standard $AgNO_3$ solution.

LEAD, Pb (*Plumbum*); atomic weight 207·21

LEAD is both divalent and tetravalent as regards its compounds. The metal when freshly cut is bluish-grey in colour; a metal soft in character. Melting point 327° C., boiling point 1525° C., specific gravity 11·35, readily dissolved by hot dilute nitric acid. Lead enters into several alloys, such as: type metal, consisting of lead, antimony and tin; bearing metal, a combination of lead and antimony alone, or, sometimes, lead, antimony and tin; shot metal, which consists of lead 99·6 per cent with small amounts of arsenic. In conjunction with bismuth and tin, such combinations as Newton's alloy, Rose's alloy, Wood's alloy and several others are produced.

The chief minerals of lead are the following:

Galena or *Blue Lead*. PbS. Cryst. system cubic, the common form being a cube, but may also occur in massive and in granular conditions. Gives a lead-grey streak and has a metallic lustre. Hardness 2·5–2·7; specific gravity 7·2–7·6. Consists of lead 86·6 per cent, sulphur 13·4 per cent. Small amounts of silver sulphide are nearly always associated with this ore. In Great Britain it is found in Cornwall, Devon, Derbyshire, Yorkshire, Westmorland, Cumberland and Durham; also at Leadhills in Lanarkshire and in the north of Scotland.

Minium, or *Native Red Oxide*. A product found as a dusty fine powder, usually orange-red in colour and gives an orange-yellow streak. Lustre usually dull and greasy. Hardness 2–3; specific gravity 7·6. Chemical formula, Pb_3O_4. Occurs at Alston in Cumberland and at Snailbeach mine in Shropshire, Weardale in Co. Durham and in Co. Wicklow, Eire.

Anglesite, $PbSO_4$, lead sulphate, so called as it was first found in Anglesey, North Wales. A native sulphate of lead, or lead-vitriol. Frequently occurs with galena. The cryst. system is rhombic, a common form being that of rhombic prisms. Colour generally white, but may be tinged with grey, yellow, green and occasionally blue. Streak colourless, fracture conchoidal, very brittle. Soluble in water. Hardness 2·75–3·0; specific gravity 6·12–6·39. Composition: lead oxide 73·6 per cent and sulphur trioxide, SO_3, 26·4 per cent. Found in Derbyshire, Cumberland, at Leadhills, Lanarkshire, and in the lead mines of Missouri and Wisconsin, U.S.A.

Cerussite, $PbCO_3$, a lead carbonate. Cryst. system rhombic, commonly found as right rhombic prisms, cleavage runs parallel to the faces of the prism, but frequently imperfect, crystals often found twinned. Colour greyish-white, occurring in plumbi-ferrous deposits, usually in the upper portions. May be looked upon as a decomposition mineral of galena. Lustre adamantine to vitreous. Streak colourless, fracture conchoidal. A brittle mineral, with hardness 3–3·5 and specific gravity 6·46–6·48. Composition: lead oxide, PbO, 83·5 per cent; carbon dioxide, CO_2, 16·5 per cent. Soluble in dilute nitric acid with effervescence due to the escape of CO_2. Found in Cornwall, Devon, Derbyshire, Shropshire, near Aberystwyth in Mid-Wales and Yorkshire.

Pyromorphite, $3Pb_3P_2O_8.PbCl_2$. Cryst. system hexagonal; common form, hexagonal prisms with basal planes. Crystals frequently aggregated. Colour often green, hence the name green lead ore; also found brown and yellow. Lustre resinous, streak white or yellowish-white. Hardness 3·5–4; specific gravity 6·5–7·1. A phosphate and chloride of lead, sometimes associated with phosphate of lime. Composition: lead phosphate 87–90 per cent; chloride of lead 10–11 per cent. When phosphate of lime is also present, the lead phosphate may vary from 57 to 80 per cent, the chloride from 8 to 10·5 per cent and the lime phosphate from 8 to 22 per cent. Small amounts of arsenic acid, H_3AsO_4, may also occur. When heated in a closed tube the mineral gives a sublimate of lead chloride. In the bunsen flame the mineral fuses, colouring the flame bluish-green. On charcoal the mineral fuses forming a globule, but does not become reduced to metallic lead, the charcoal being coated with yellow lead oxide and white lead chloride. In the British Isles the mineral has been found at St. Hilary and other mines in Cornwall, at Beeralston in Devon, Bonsall Moor, Derbyshire, near Middleton, in Teesdale, Co. Durham, Coldbeck Fells, Cumberland; also in Lanark and Dumfries in Scotland, etc.

Mimetite, $Pb_2As_2O_7.PbCl_2$, an arsenate and chloride of lead. Cryst. system hexagonal, colour frequently pale yellow or brownish, also white. Lustre resinous. Hardness 3·5; specific gravity 7–7·25. A variety of mimetite is kampylite, having curved crystals, and is found at Drygill in Cumberland. Other places in the United Kingdom where mimetite has been found are at Carrock Fells, Cumberland, Grassington, Yorkshire, and in Teesdale, Co. Durham. It occurs in many lead mines in the United States.

Crocoisite, $PbCrO_4$, a lead chromate. Cryst. system monoclinic. Usual form modified oblique rhombic prism. Sometimes occurs granular or in a columnar condition, colour various shades of red. Streak, orange-yellow. Hardness 2·5–3; specific gravity 5·9–6. Composition: oxide of lead 68·9 per cent; chromic acid, CrO_3, 31·1 per cent. When heated in a closed tube it crackles and turns blackish, returning to the original colour on cooling. When heated on charcoal in the blowpipe reducing flame, metallic lead is formed, the charcoal being coated with lead and chromium oxides. A borax bead is coloured emerald-green. The mineral is found in Silesia, Mursjrsk, in the Ural mountains, and in the island of Luzon, one of the Philippine group.

Wulfenite, $PbMoO_4$, lead molybdate. Cryst. form tetragonal, common form tetragonal prisms and pyramids, also found granular and massive. Colour, various shades of yellow and orange, also yellowish-grey, grey-white and occasionally orange-red; fracture, subconchoidal. Hardness 2·75–3; specific gravity 6·03–7·01. Composition: lead oxide 61·5 per cent; molybdic acid, H_2MoO_4, 38·5 per cent.

The borax bead in the oxidizing flame is colourless; in the reducing flame opaque and black; occasionally gives a dirty-green with black specks. On charcoal, when mixed with sodium carbonate, it is reduced to metallic lead. When treated with dilute hydrochloric acid and a scrap of zinc it is converted into a blue compound, MoO_22MoO_3, known as molybdenum molybdate, which is soluble in water, but precipitated on the addition of a saline solution. In the British Isles it is found at Lackentyre, Kirkcudbright; but the mineral yielding very fine specimens is found in Arizona, U.S.A.

Cromfordite or *Phosgenite*, $PbCl_2PbCO_3$, a compound of lead chloride and carbonate. Colour, white, grey and sometimes yellowish-white. Hardness 2·75–3; specific gravity 6–6·3. On the addition of nitric acid, it dissolves with effervescence due to the evolution of CO_2. Composition: lead chloride 51 per cent; lead carbonate 49 per cent. Originally found at Cromford, near Matlock, Derbyshire; also near Elgin in Scotland.

Qualitative Tests

Salt used: lead nitrate, $Pb(NO_3)_2$.

1. Hydrochloric acid causes a white precipitate of lead chloride to form; insoluble in ammonia:

$$Pb(NO_3)_2+2HCl=PbCl_2+2HNO_3$$

2. Sulphuretted hydrogen gives a black precipitate of lead sulphide:

$$Pb(NO_3)_2+H_2S=PbS+2HNO_3$$

3. Ammonium sulphide also causes a black precipitate of lead sulphide to form:

$$Pb(NO_3)_2+(NH_4)_2S=PbS+2NH_4NO_3$$

4. Potassium chromate causes a yellow precipitate of lead chromate to form; insoluble in acetic and very dilute nitric acids, but soluble in strong boiling nitric acid:

$$Pb(NO_3)_2+K_2CrO_4=PbCrO_4+2KNO_3$$

5. Sulphuric acid causes a white precipitate of lead sulphate to form. This is slightly soluble in water, but is made entirely insoluble on the addition of alcohol. Decomposed by strong boiling hydrochloric acid and easily soluble in solutions of ammonium acetate containing an excess of ammonium hydroxide:

$$Pb(NO_3)_2+H_2SO_4=PbSO_4+2HNO_3$$

6. Potassium and sodium hydroxides cause a white precipitate of lead hydroxide to form; soluble in excess, causing the formation of potassium and sodium plumbates, K_2PbO_2 or Na_2PbO_2:

$$Pb(NO_3)_2+2KOH=Pb(OH)_2+2KNO_3$$

Quantitative Assays

The most common method for the estimation of this metal is the titration of the solution of the sulphate in ammonium acetate with standard ammonium molybdate, an excess of the latter being shown by a yellow coloration imparted to spots of tannin solution when brought in contact with a few drops of the solution under examination on a white porcelain tile or spot plate. The method which is given below is very suitable for quantities of lead exceeding 0·2 gram, but for lesser quantities the thiosulphate method is preferable.

It is often impossible to obtain a representative charge of ashes containing metallic lead for wet assay, so that charges of 100 gram are taken for dry assay, as described on page 18.

AMMONIUM MOLYBDATE METHOD

Dissolve a portion of the material containing between 200 and 700 mg. in aqua regia; evaporate slowly until nearly dry and then add carefully 7–15 ml. strong sulphuric acid. Replace the beaker on the hot plate and leave until fuming strongly. Cool, add 20 ml. cold distilled water, stir, make up to 100 ml. with boiling water, and boil for 10 minutes.

Allow the trial to stand cold for at least 4 hours, and preferably overnight. Filter through paper pulp; wash with normal sulphuric acid, and return the pulp and precipitate to the beaker. Add about 5 gram of ammonium acetate and about 100 ml. hot water, boil for 10–15 minutes, and refilter through pulp. Return filtrate to beaker, bring to the boil, adjust bulk to about 250–300 ml., and titrate with standard ammonium-molybdate solution, using drops of dilute (about 0·1 per cent) tannin solution as outside indicator.

THIOSULPHATE METHOD

This method is based on the estimation of the available oxygen in the chromate salt of lead.

The procedure is similar to the molybdate method up to the extraction of the lead sulphate with ammonium acetate. To the boiling solution add 10 ml. of saturated potassium bichromate, and continue to boil until the yellow precipitate has turned to brick-red. Allow to stand hot until the lead chromate has settled, and then filter through a wad of paper pulp in a Gooch crucible, using a moderate suction and washing thoroughly with hot water. Reject filtrate, rinse out pressure flask, and replace Gooch. Dissolve precipitate on pulp with a jet of acidulated sodium-chloride solution, and allow filtrate to be sucked into the flask. Transfer filtrate to a 400-ml. conical flask, add 3 gram of KI, and titrate to a green or bright yellow colour (the KI in excess often precipitates the $PbCl_2$ as PbI_2) with N/10 sodium thiosulphate, using starch paste as indicator (1 ml.$=$0·0069 gram Pb).

DRY ASSAY (for lead ashes or drosses)

After calculating the proportions of metals and fines, weigh out a representative 100-gram charge and mix intimately with the following:

Potassium ferrocyanide	30 gram
Sodium carbonate (anhydrous)	20 „
Borax	10 „

Transfer to a size " G " (Battersea) crucible and place in the coke fire. When thoroughly molten and quiescent, remove from the fire and allow to cool in the crucible.

When quite cold, break away the pot, clean the button of metal and weigh. Tin and antimony may be estimated in the button and the lead taken by difference, but in view of the considerable difficulty with which a truly representative sample of such material is obtained, it would seem unreasonable to go to this trouble unless the figures are actually required.

MERCURY, Hg (*Hydrargyrum*); atomic weight 200·6

MERCURY is a divalent element and forms two series of salts, viz. mercurous and mercuric. Metallic mercury has a specific gravity of 13·6, and under normal conditions is a silver-white liquid. It becomes a solid at −39° C., and has a boiling point of 357·3° C. When treated with cold dilute nitric acid mercury dissolves forming mercurous nitrate; and, when treated with hot concentrated acid, mercuric nitrate. It is insoluble in hydrochloric acid. Mercurous oxide, Hg_2O, is a black powder while mercuric oxide, HgO, is bright red. The following are the chief sources of this element:

Native Mercury, otherwise commonly called quicksilver. Cryst. system when frozen cubic, the crystals being octahedra. In nature, occurs as small globules, lustre metallic, specific gravity 13·56. Sometimes small amounts of silver are associated with it. Another variety known as *Mercury Amalgam* is found native and is silver-white in colour. A brittle mineral, with a conchoidal or uneven fracture. Hardness 3–3·5; specific gravity 10·5–14·1. A combination of mercury and silver, Ag_2Hg_2: mercury 65·2 per cent, silver 34·8 per cent. When heated on charcoal the mercury volatilizes, and a globule of silver remains; when heated in a closed tube the mercury sublimes. Mercury amalgam dissolves easily in nitric acid.

Cinnabar, HgS, mercury sulphide. This is the only mercury ore of any importance. Cryst. system hexagonal. Usually occurs granular or massive, sometimes forms crusts. Colour, red or brownish-red;

streak scarlet. Hardness 2–2·5; specific gravity 8·99. Composition: mercury 86·2 per cent, sulphur 13·8 per cent. When heated in a closed tube, gives a black sublimate of mercury sulphide; when heated in an open tube, gives a sublimate of metallic mercury; also some black sulphide and fumes of SO_2.

Qualitative Tests

Mercury(ous)

Salt used: mercury(ous) nitrate, $HgNO_3$.

1. Hydrochloric acid gives a white precipitate of mercurous chloride, HgCl, calomel:

$$HgNO_3 + HCl = HgCl + HNO_3$$

Insoluble in cold hydrochloric acid and nitric acid, but dissolves slowly on boiling. It is decomposed by ammonia, yielding a black precipitate of mercurous ammonium chloride, NH_2Hg_2Cl.

2. Sulphuretted hydrogen, H_2S, gives a black precipitate consisting of mercuric sulphide and metallic mercury. Insoluble in dilute acids and solutions of potassium cyanide:

$$2HgNO_3 + H_2S = HgS + Hg + 2HNO_3$$

3. Ammonium sulphide, $(NH_4)_2S$, brings down a black precipitate almost entirely composed of mercurous sulphide; soluble in dilute acids, and in potassium cyanide solution:

$$2HgNO_3 + (NH_4)_2S = Hg_2S + 2NH_4NO_3$$

4. Potassium and sodium hydroxides, when added to a solution containing a mercurous salt, give a black precipitate of mercurous oxide, insoluble in excess. A test distinctive from mercuric salts, which on the addition of either of the above reagents give a yellow precipitate of mercuric oxide:

$$2HgNO_3 + 2KOH = Hg_2O + H_2O + 2KNO_3$$

5. When a strip of copper foil is warmed in a test tube with a mercury compound which has been acidified with hydrochloric acid, a coating of metallic mercury is deposited on the foil. On removing the foil and drying between two pieces of filter paper, and then gently rubbing the surface of the foil, a characteristic silvery appearance is obtained. When native amalgam is rubbed on copper foil the same silvery appearance is produced, an excellent test for both mercurous and mercuric salts.

Mercury(ic), lead, bismuth, copper, cadmium, arsenic, antimony, tin(ous) and (ic), gold, platinum, molybdenum and tungsten form a series of metals, the sulphides of which are insoluble in dilute HCl, and are precipitated on the addition of H_2S in the presence of HCl. The series is further divided into two sub-groups, A and B.

A. This sub-group comprises such metals as mercury(ic), lead(ic), bismuth, copper and cadmium, whose sulphides are insoluble in HCl and $(NH_4)_2S$, but are precipitated by H_2S.

B. This sub-group comprises such elements as arsenic, antimony, tin, gold and platinum, the sulphides of which are insoluble in dilute acids, but are dissolved by alkalies, and, being precipitated by H_2S, are dissolved by $(NH_4)_2S$ solution.

Mercury(ic)

Salt used: mercuric chloride, $HgCl_2$.

1. Hydrochloric acid gives no precipitate or reaction which distinguishes mercurous from mercuric salts.
2. Sulphuretted hydrogen in the presence of hydrochloric acid yields a black precipitate of mercuric sulphide which is insoluble in ammonium sulphide and nitric acid:

$$HgCl_2+H_2S=HgS+2HCl$$

3. Ammonium sulphide also gives a black precipitate of mercuric sulphide. Potassium and sodium sulphide solutions in the presence of potassium and sodium hydroxides dissolve the black precipitate completely:

$$HgCl_2+(NH_4)_2S=HgS+2NH_4Cl$$

4. Potassium and sodium hydroxides cause a yellow precipitate of mercuric oxide to form; insoluble in excess. The solution should not be very acid before the addition of the alkali:

$$HgCl_2+2KOH=HgO+H_2O+2KCl$$

5. Potassium chromate gives a red precipitate of mercuric chromate; soluble in excess:

$$HgCl_2+K_2CrO_4=HgCrO_4+2KCl$$

6. Potassium iodide causes a scarlet precipitate of mercuric iodide to form; soluble in excess as mercuric potassium iodide:
   (a) $HgCl_2+2KI=HgI_2+2KCl$
   (b) $HgI_2+2KI=HgK_2I_3$
7. The copper test mentioned under mercurous salts acts in a similar way with mercuric compounds, by the deposition of metallic mercury.

8. Mercuric ammonium chloride (infusible white precipitate) is formed when ammonia is added to a solution of mercuric chloride:

$$HgCl_2+2NH_2=(NH_2Hg)Cl+NH_4Cl$$

Quantitative Assay

While this metal is not so common as the other Group II metals, or some of the precious metals, its rarity does not justify exclusion from this work. A fairly satisfactory method exists for the electrolytic determination of mercury and this is described below. However, by far the safest method is that of Rose, which is as follows.

Take a piece of combustion tubing about 15 inches in length and of about $\frac{3}{8}$ inch internal diameter and seal one end. Place in the sealed end about 2 inches of coarse raw magnesite. Add 15 gram of the ore, which has been previously mixed with 5 gram of freshly ignited CaO, and push a small plug of asbestos down the tube to hold the contents in position. Draw out the open end of the tube and bend at right angles. Place the tube in a combustion furnace, so that the end which has been drawn out hangs downward and stands in a beaker of water at such a height that the tip of the tube is just immersed. Heat the tube gently at first, commencing at the end nearest the beaker, gradually working backwards and increasing the temperature until the whole tube is red hot. Mercury vapour is driven off from the ore and condenses in the water, the CO_2 from the magnesite helping to drive any mercury from the neck of the tube into the beaker. Shake the beaker so as to obtain the mercury in one globule, pour off the water, and collect the globule on a piece of blotting-paper, dry in a desiccator, and weigh.

ELECTROLYTIC METHOD

The mineral is dissolved in a mixture of dilute HNO_3 and HCl, and the mercury precipitated with H_2S. Boil the precipitate with dilute $NaOH$ until the dark colour becomes pale. The insoluble lead is filtered off and the mercury, which is present in solution as a complex salt, is reprecipitated from the solution by adding ammonium nitrate and boiling until all the ammonia is expelled. The precipitate is then dissolved in nitric and hydrochloric acids, warming slightly to effect solution, and then diluted to 100 ml.

The solution is now electrolysed, using a sheet of copper for a cathode. It is essential to pass the current before the beaker is placed in position, otherwise the copper will displace the mercury in the solution, instead of the latter being displaced by electrolysis. The solution should be tested for copper with ammonia after the assay is finished

(3 hours), and should any be present the assay is spoiled. The cathode is washed with water and alcohol, dried in the desiccator, and weighed. Current—0·055–0·10 ampere; voltage—3·5–5 volts.

BISMUTH, Bi; atomic weight 209·0

THIS element is trivalent and pentavalent. The metal resembles tin and has a reddish tint. The specific gravity is 9·78; melting point 269° C., boiling point 1436° C. When heated on charcoal, yields yellow bismuth oxide, Bi_2O_3. Quite soluble in nitric acid, but almost insoluble in hydrochloric acid. It forms two oxides, Bi_2O_3 and Bi_2O_5. Bismuth oxide and the hydroxide are readily soluble in nitric, hydrochloric and sulphuric acids. When bismuth oxide is fused with potassium cyanide, metallic bismuth is produced.

Native Bismuth. Cryst. system hexagonal. Is found in rhombohedra, having a cubical appearance, and in various forms, sometimes granular, foliated or massive; colour, white, having a slight red tinge. Easily tarnished in the air. Lustre metallic, a brittle metal when cold, but becomes somewhat malleable on heating. Hardness 2–2·5; specific gravity 9·7–9·8. The native bismuth frequently contains traces of arsenic, sulphur and tellurium. Easily dissolves in nitric acid. Nearly all metallic bismuth and its compounds originate from native bismuth. In the British Isles, native bismuth is found near St. Ives, Cornwall; also at Coldbeck Fells in Cumberland.

Bismuthine, Bi_2S_3. Cryst. system rhombic. Colour, lead-grey; occurs at Brandy Gill, Cumberland; also in Cornwall. Quite a rare mineral occurring in small amounts and of no commercial value.

An oxide of bismuth, known as *Bismuth Ochre*, B_2O_3, also occurs in small amounts, but is of no value as a pigment.

Qualitative Tests

Salt used: bismuth nitrate, $Bi(NO_3)_3$.

1. On the addition of a little hydrochloric acid, a white precipitate of bismuth oxychloride, BiOCl, may form. This only occurs in dilute solutions in the presence of a small amount of hydrochloric acid. On the addition of more acid, the white precipitate dissolves rapidly if the liquid is warmed. The same white precipitate forms when a solution of bismuth chloride is poured into water.
2. Sulphuretted hydrogen in the presence of HCl gives a dark brownish-black precipitate of bismuth sulphide, Bi_2S_3; insoluble in cold dilute acids and alkali, but soluble in boiling nitric acid:

$$2Bi(NO_3)_3 + 3H_2S = Bi_2S_3 + 6HNO_3$$

3. The same brownish-black precipitate is produced on the addition of ammonium sulphide:

$$2Bi(NO_3)_3+3(NH_4)_2S=Bi_2S_3+6NH_4NO_3$$

4. Potassium and sodium hydroxides cause a white precipitate of bismuth hydroxide, $Bi(OH)_2$, to form. The precipitate is somewhat soluble in hot concentrated alkali, and on standing the solution goes yellow, with the formation of bismuth hydroxide, especially if boiled:

$$Bi_2(NO_3)_3+3KOH=Bi(OH)_3+3KNO_3$$

5. Potassium chromate produces a yellow precipitate of bismuth oxychromate, soluble in dilute nitric acid, but not in potassium hydroxide (distinction from lead chromate).
6. A bead of metallic bismuth is formed when mixed with sodium carbonate and heated on charcoal with the blowpipe. This is surrounded by an incrustation of oxide; dark orange-yellow when hot, and pale-yellow when cold.

The chief alloys of bismuth are:

Newton's alloy: Bi 50 per cent, Pb 31·25 per cent, Sn 18·75 per cent, melting point 95° C.

Rose's alloy: Bi 50 per cent, Pb 28·1 per cent, Sn 24·64 per cent, melting point 100° C.

Darset's alloy: Bi 50 per cent, Pb 25 per cent, Sn 25 per cent, melting point 93° C.

Wood's alloy: Bi 50 per cent, Pb 24 per cent, Sn 14 per cent, Cd 12 per cent, melting point 66–70° C.

Lipowitz's alloy: Bi 50 per cent, Pb 27 per cent, Sn 13 per cent, Cd 10 per cent, melting point 60° C.

All these are known as fusible alloys, because of their low melting points.

Quantitative Assays

Bismuth is usually estimated gravimetrically, either as the oxide Bi_2O_3 or as the oxychloride BiOCl. For extremely small quantities a colorimetric method can be used with advantage, while a volumetric method based on the titration of the oxalic acid equivalent with potassium permanganate is also available. The preliminary treatment of the mineral is, however, essentially the same in all cases, and is as follows:

A convenient weight of the finely ground ore is dissolved in aqua regia, evaporated to low bulk and heated till fuming with H_2SO_4.

When cold, the paste is taken up with about 15 ml. of cold distilled water, well stirred, and then made up to about 150 ml. with boiling water, boiled for 10 minutes, and allowed to settle for at least 4 hours in the cold (preferably overnight).

The lead sulphate is removed by filtering the solution through paper pulp and washing the pulp and precipitate with cold normal H_2SO_4. The filtrate is transferred to a 400- or 500-ml. conical beaker and H_2S passed through for half an hour. The precipitate will consist of the sulphides of copper, bismuth, possibly cadmium, and also the metals of Group IIA (arsenic, antimony and tin). The precipitate is collected on paper pulp, washed with hot water, and returned to the beaker. About $\frac{1}{2}$ gram of sodium dissolved in 100 ml. of hot water is added and the beaker placed on the hot plate for about 10 minutes, by which time the Group IIA sulphides will be dissolved. The insoluble sulphides and the pulp are again filtered through pulp, the combined wads being returned to the beaker once more. The pulp is now boiled with dilute H_2SO_4 (20 per cent by volume), which dissolves the CdS and bismuth, leaving the copper unattacked. A further filtration through pulp removes this metal, and the filtrate, which might contain some zinc, is neutralized with ammonia, made just acid with 50-per-cent H_2SO_4 and 10 ml. added in excess. H_2S is again passed through the solution for half an hour, and, after settling, the combined precipitates are filtered off, and washed with water containing H_2S. The precipitate is washed back into the beaker and the paper is rinsed with hot dilute HNO_3 and bromine water, the washings being collected in the beaker. A few cubic centimetres of HCl are added and the solution is evaporated to low bulk. If no cadmium is present, the solution is made alkaline with ammonia and a slight excess of ammonium carbonate is added to precipitate the Bi as carbonate. This is filtered off, ignited, and weighed as Bi_2O_3.

Where cadmium is present, the solution is evaporated to dryness to remove the HNO_3, 5 ml. HCl is added to dissolve the residue, then the acid is neutralized with ammonia, using methyl orange as indicator. Dilute HCl is now added drop by drop until the pink colour returns, at which point a large excess of boiling water is added to convert the soluble bismuth chloride to insoluble oxychloride. After settling, the precipitate is filtered through a weighed sintered glass crucible, Grade G.3, dried for 2 hours at 105° C. and weighed.

An alternative method for the removal of copper, where no zinc or cadmium is present, as in, for example, copper matte, is as follows:

To the filtrate from the lead sulphate, add ammonia in slight excess until the hydrated copper is just dissolved; KCN is added to discharge the blue colour and dissolve any iron present and the solution is gassed with H_2S for half an hour. In the presence of KCN neither iron nor copper will be precipitated and the bismuth can be filtered off and treated as above, the assay in the case of materials low in Bi being preferably completed colorimetrically, as shown on the next page.

The following method for the determination of bismuth in lead ores combines both dry and wet assays.

40 gram of ore is smelted with 30 gram of soda ash and 5 gram of argol* in a wrought-iron crucible. The metal is poured and the cleaned button flattened out and cut into strips. 10 gram of the cuttings is dissolved in 80 ml. of water and 20 ml. of HNO_3 and boiled for 10 minutes to precipitate the bulk of the Sn and Sb and some As; 5 ml. of N/10 NaCl is added to precipitate the Ag whilst boiling. The lead is then precipitated by adding gradually to the boiling solution 50 ml. of hot N/2 H_2SO_4 (10 ml. 10N. H_2SO_4 and 40 ml. water). 30 ml. of the 10N. H_2SO_4 is now added, and, after coooling thoroughly, the solution is allowed to stand an hour, filtered and washed with normal H_2SO_4.

To prevent basic bismuth salts being carried down with the silver and lead, it is important that the above details be followed accurately.

The filtrate is now neutralized with ammonia and a drop or so added in excess, a drop of methyl orange being used as indicator, then drops of 1 : 3 HCl are added till the indicator turns pink again. The solution is boiled, allowed to remain warm for half an hour, and filtered, washing once or twice with hot water. It is as well to readjust the acidity of the filtrate, boil, and allow to stand to make sure that all the bismuth has been precipitated.

The oxychloride precipitate and the filter are returned to the beaker, 20 ml. of 10N. H_2SO_4 added and the whole boiled gently and again cooled thoroughly. Avoid pulping the filter. The solution is filtered into a 250-ml. measuring flask, the paper being squeezed with a flat-ended rod on the sides of the beaker and washed several times in this fashion with N. H_2SO_4.

A quantity of the solution equal to 0·0005–0·0015 gram Bi is put into a Nessler tube with 5 ml. N. KI and 10 drops of an N. solution of SO_2 and made up to 100 ml. with water; it is compared with the standard containing the same quantities of acids and KI, and titrated with standard Bi solution till it matches the test.

Solutions required:

Standard Bismuth Solution. 0·1 gram pure Bi metal in 10 ml. conc. H_2SO_4 and diluted to a litre.

N. KI: 163 gram per litre.

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* Crude tartar from wine fermentation, containing 60–75% of potassium bitartrate.

N. sulphurous acid: 1 part of saturated solution to 2½ water.
N/10 NaCl: 5·8 gram per litre.

Note.—The normality of the solution need not be exact.

COPPER, Cu (*Cuprum*); atomic weight 63·57

THIS element is both monovalent and divalent. Copper is red in colour and is hard and ductile. It melts at 1082–4° C. and boils at 2310° C. When in the presence of air and moisture the metal becomes covered with green basic carbonate called "Patina." Cuprous oxide, Cu_2O, is red, while cupric oxide, CuO, is black. Copper dissolves readily in hydrochloric and nitric acids.

Borax beads containing copper minerals are green when heated in an oxidising flame. When cold the bead is blue. When heated in the reducing flame the bead is colourless to green when hot and red-opaque when cold. With microcosmic salt (hydrogen-sodium-ammonium phosphate) in the oxidizing flame: the bead is green when hot, blue when cold. In the reducing flame the bead is pale yellowish-green when hot; pale blue, almost colourless but occasionally ruby-red, when cold.

Native Copper. Cryst. system cubic, the usual form octahedra, twinned crystals often occurring. Sometimes found in thin plates, occupying narrow fissures. Colour, copper-red. Lustre metallic. Hardness 2·5–3; specific gravity 8·8. Composition: copper only, but sometimes there are traces of silver. Is easily fusible, and becomes coated with cupric oxide, CuO, on cooling. Dissolves easily in dilute nitric acid, forming cupric nitrate and giving off nitric oxide. On neutralizing with ammonia, gives a blue solution. Most commonly found in the older volcanic rock formations.

Cuprite, Cu_2O, red oxide of copper. Cryst. system cubic; commonly found in two forms, octahedra and rhombic-dodecahedra; usually found massive or granular. Occurs in different shades of red; a brittle mineral with conchoidal and uneven fracture. Hardness 3·5–4; specific gravity 5·8–6·15. Composition (cuprous oxide); copper 88·8 per cent, oxygen 11·2 per cent. Found in several old mines in Cornwall, such as Huel Gorland and Carn Brea. In Spain, Chile, Peru, near Lake Superior and in South Australia.

Copper Pyrites, also known as *Chalcopyrite*, $CuFeS_2$, a sulphide of copper and iron. Cryst. system tetragonal, a rather brittle mineral, fracture conchoidal. Lustre metallic. Colour, brass-yellow. Hardness 3·5–4; specific gravity 4·1–4·3. Composition: copper 32·5–34·0 per cent, iron 29·75–31·25 per cent, sulphur 34–36 per cent. When heated in a closed tube gives a sublimate of sulphur. In the oxidizing flame, gives a reddish-green borax bead, due to both copper and iron; and in the reducing flame, a green bead when hot, nearly colourless when cold. One of the most important ores of copper. Found in many old Cornish mines associated with tin stone, galena and blende; also near Swansea in South Wales; in Lancashire in the Coniston copper mines situated on the Old Man Mountain, Alston Moor; Goldscobe mine, Vale of Newlands, Cumberland; Kirkcudbright, Scotland; and in many parts of the United States, in Canada and Australia.

Tenorite, also known as *Melaconite*. Black cupric oxide, CuO. Usually found as black powdery masses or spheroidal aggregations, somewhat like a bunch of grapes. Soluble in hydrochloric, nitric and sulphuric acids. Hardness 3; specific gravity 6·25. Has been found at Roughtengill in Cumberland. Very common in the copper mines of the Mississippi valley, U.S.A.

Copper Glance, also known as *Redruthite* or *Vitreous Copper Ore*. Cryst. system rhombic or ortho-rhombic, frequently twinned showing rhombic prisms. Colour, dark lead-grey. Lustre metallic. Fracture conchoidal. Hardness 2·5–3; specific gravity 5·5–5·8. A copper sulphide, Cu_2S, copper 79·8 per cent, sulphur 20·2 per cent. Traces of iron often present. When treated with hot nitric acid leaves a deposit of sulphur. In Great Britain occurs at St. Just, Cornwall; also in Ayrshire; in Kerry in the Kenmare district; and in Saxony and Siberia. The mineral also occurs in several South American countries such as Bolivia, Chile and Peru, and in the North American states of Arizona, Maryland and Virginia.

Tetrahedrite, also called grey-copper. Cryst. system cubic; common form tetrahedra, often twinned. Colour, sometimes steel-grey, at other times very dark grey or black. Lustre metallic; a rather brittle mineral mostly of uneven fracture, but also found subconchoidal. Hardness 3·45; specific gravity 4·5–5·1. A copper and antimony sulphide, $4Cu_2S.Sb_2S_3$, copper 46·8 per cent, antimony 29·6 per cent, sulphur 23·6 per cent. The copper is often replaced by iron, zinc or mercury, and the antimony by about 7 per cent of arsenic. When heated in a closed tube, the mineral fuses, giving a dark-red sublimate of antimony sulphide. When heated in an open tube gives a white sublimate, giving off fumes of SO_3; when heated on charcoal, the mineral fuses giving incrustations of different colours. If lead is present then the incrustation is yellow. If antimony or arsenic is present the incrustations are white.

Bournonite also known as *Endellionite*. Cryst. system rhombic;

common form modified rectangular prisms, frequently twinned. Colour, steel-grey or blackish-grey. Lustre metallic; a brittle mineral having an uneven or conchoidal fracture. Hardness 2·5–3·0; specific gravity 5·7–5·9. A copper, lead and antimony sulphide, $(PbS)_4Sb_2S_3+(Cu_2S)_2Sb_2S_3$; copper 12–15 per cent, antimony 24–29 per cent, lead 39–43 per cent, sulphur 18–20 per cent. Found in several mines in Cornwall, near Liskeard; also in Bolivia and Chile.

Chalcanthite, $CuSO_4.5H_2O$, also known as *Cyanosite*, blue copper sulphate or blue vitriol. Cryst. system triclinic. Colour, light blue, sometimes greenish-blue. Lustre vitreous; a brittle mineral found sometimes amorphous, at other times incrusting; also found in stalactitic form. Composition: copper oxide 31·8 per cent, SO_3 32·1 per cent, water 36·1 per cent. When heated in a closed tube, moisture is first given off, then sulphuric acid, which can be tested by holding a damp piece of blue litmus paper over the mouth of the tube. Soluble in water. The steel blade of a penknife, when allowed to remain a short time in the solution, becomes coated with metallic copper. When heated with a flux on charcoal in the reducing flame of a blowpipe the powdered mineral is reduced to metallic copper. The theoretical composition of copper sulphate, as manufactured, is CuO 31·86 per cent, SO_3 32·06 per cent, H_2O 36·08 per cent. The native sulphate is formed by the oxidation of copper pyrites.

Malachite or green copper carbonate, $CuCO_3.Cu(OH)_2$. Cryst. system monoclinic, often found massive, sometimes granular or stalactitic, or may occur with both large spheroidal surfaces and small spheres or aggregates. Colour, various shades of green. Hardness 3·5–4; specific gravity 3·7–4. Composition: copper oxide 71·9 per cent, carbon dioxide 20 per cent, moisture 8·2 per cent. The mineral easily dissolves in acids, giving off CO_2. When heated it fuses and colours the bunsen flame emerald-green; gives a green bead with borax. Found at Roughtengill in Cumberland and in Cornwall. Occurs in large quantities at Nijni-Tagnilsk, Siberia, in several of the North American states and Australia.

Other minerals containing copper are:

Azurite. Colour, deep blue, a copper carbonate very similar in composition to malachite. $2.CuCO_3.Cu(OH)_2$.

Dioptase. Hydrated copper silicate, $CuSiO_3.H_2O$. Hardness 5; specific gravity 3·2–3·3. Colour, green.

Chrysocolla. Hydrated copper silicate, $CuSiO_3.2H_2O$. Hardness 2–4; specific gravity 2·2–2·3. Often contains many impurities, an approximate analysis being: copper oxide 28–44 per cent, silica 26–40 per cent, water 16–31 per cent. Found at Coldbeck Fells, Cumberland.

Atacamite. Copper oxychloride, $CuCl.3Cu(OH)_2$. Composition: copper oxide 53·6 per cent, copper chloride 30·2 per cent, water 16·2 per cent. Hardness 3–3·5; specific gravity 4–4·3.

Libothenite. Hydrous copper phosphate $(CuOH)CuPO_4$.

Phosphochalcite. Another copper phosphate, $Cu_6P_2O_{11}.3H_2O$.

Qualitative Tests

Salt used: copper sulphate, $CuSO_4.5H_2O$.

1. Hydrochloric acid brings about no reaction.
2. Sulphuretted hydrogen and ammonium sulphide give black precipitates of copper sulphide, CuS, insoluble in dilute acids, but soluble in strong nitric acid:

   (i) $CuSO_4 + H_2S = CuS + H_2SO_4$

   (ii) $CuSO_4 + (NH_4)_2S = CuS + (NH_4)_2SO_4$
3. Potassium and sodium hydroxides in the cold give a light-blue precipitate of cupric hydroxide, $Cu(OH)_2$, which on heating changes to a blue-black precipitate of cupric oxide. The light-blue cupric hydroxide is insoluble in excess of alkali.

   $$CuSO_4 + 2NaOH = Cu(OH)_2 + Na_2SO_4$$
4. Ammonium hydroxide gives a strong light-blue precipitate, soluble in excess, to a deep-blue solution of tetrammonium cupric-sulphate $(NH_3)_4CuSO_4.H_2O$.
5. Potassium ferrocyanide causes a brownish-red precipitate of copper-ferrocyanide to form which is insoluble in dilute acids, but is decomposed by potassium or sodium hydroxides:

   $$2CuSO_4 + K_4Fe(CN)_6 = Cu_2Fe(CN)_6 + 2K_2SO_4$$
6. Potassium thiocyanate, KCNS, causes a black precipitate of cupric thiocyanate to form in concentrated solutions which are only slightly acid, otherwise a dark coloration will be produced:

   $$CuSO_4 + 2KCNS = Cu(CNS)_2 + K_2SO_4$$

Copper compounds impart a bright emerald-green to the bunsen flame, and, when hydrochloric acid is present, a blue inner flame will appear. With the blowpipe, when using the oxidizing flame, copper compounds give with the borax bead a green bead when hot and a blue bead when cold. In the reducing flame the bead is brick-red and opaque. With microcosmic salt, copper gives a blue bead in the oxidizing flame, red in the reducing flame.

Quantitative Assays

Weigh out 0·5–5 gram of the ore into a 400-ml. squat beaker and add about 20 ml. of aqua regia. When dissolved, remove the cover and allow the solution to go nearly to dryness on the hot plate.

Cool, then, according to the amount taken for the assay, add from 5 to 20 ml. concentrated H_2SO_4; replace on hot plate and leave until fuming strongly. Cool, add about 20 ml. cold water, and stir until all the cake is softened and the acid taken up. Make up to about 150 ml. with boiling water, boil for 10 minutes and allow to stand for at least 4 hours, preferably overnight if the lead is to be estimated.

Filter through pulp, washing with normal H_2SO_4, and return filtrate to original beaker. Place in beaker a piece of aluminium sheet about 4 inches long by 1 inch wide and about 1 mm. thick, bent in the form of a triangle, and allow to boil gently on the hot plate for 1 hour. Remove triangle, and stand on watch glass; filter solution through a No. 30 Whatman paper, wash with hot water and place funnel over a 400-ml. conical beaker. Replace triangle in original beaker, and pour over it about 20 ml. of dilute HNO_3. Rinse it with hot water, remove triangle, and pour washings over the filter.

Boil filtrate until free from nitrous oxides, add slight excess of dilute ammonia (one part 0·880 ammonia to one of water). Boil for 20 minutes, add 10 ml. acetic acid, and continue boiling for a further 5 minutes.

Cool, add 3 gram potassium iodide, and titrate with N/10 sodium-thiosulphate solution, using starch paste as indicator.

The above method is very useful where the estimation of alumina is not required or where fumes of H_2S are objectionable. The standard method of separation, however, is as follows:

To the filtrate from the lead sulphate, add ammonia until neutral and acidulate with about 3 ml. HCl, or more if a large quantity of zinc is present. Pass a strong current of H_2S for about 15 minutes. The precipitate should settle readily when the gas is stopped if all the copper is down. Filter through a close-grain paper (1F Swedish or 30 or 40 Whatman), washing with hot water and water containing H_2S, being careful not to let the paper run dry. Wash the precipitate back into beaker and add two or three small crystals of sodium sulphide, about 40 ml. boiling water, and stand hot for a few minutes. Refilter through the original paper and wash well with hot water. Wash the precipitate back again into the original beaker, and place the funnel and paper over it. Now fill the paper with boiling dilute HNO_3 (about 1 : 5), adding a few ml. of bromine water. When empty, open out the paper and rinse in any residue remaining with a jet from the wash-bottle.

Bring to the boil, adding more bromine water if necessary, and, when free from nitrous fumes, titrate with iodine and thiosulphate as before. A bad end-point in the titration is usually due to incomplete removal of nitrous fumes. If the end-point is impossible to determine, the assay can be treated with a large excess of HNO_3 and evaporated on the hot plate until all the iodine is removed and the solution again a clear pale-green colour. This is titrated as before.

Copper can also be estimated in small quantities by means of the blue colour formed when solutions of the metal are treated with ammonia. No other metals but copper should be present in a solution of the mineral in HNO_3, the maximum amount of copper being about 10 mg. The solution is placed in a Nessler tube and an equivalent quantity of dilute HNO_3 added to a similar tube. Ammonia is now added to the sample test from a burette until the blue colour is formed, and then the same quantity of ammonia is added to the adjacent tube. Standard Cu solution is now added to the latter from a burette until the colour is of similar depth to that of the sample. The levels of each are adjusted and, if necessary, a further addition of the Cu solution made. It is essential to observe the details mentioned above, as any difference in the amount of ammonia added to either tube will materially alter the depth of colour rather than the shade, making matching exceedingly difficult.

Standard Copper Solution. 0·5 gram of pure electrolytic copper is dissolved in a little HNO_3 and boiled to expel brown fumes. The solution is cooled, diluted somewhat, and made just alkaline with ammonia. The solution is now diluted to 500 ml: 1 ml. will contain 1 mg. of copper.

Electrolytic Assay

A quantity of ore containing about 0·25 gram of copper is dissolved in a little HNO_3. It may be necessary to use aqua regia to effect solution, especially if much iron is present. Any silver present must be removed by the addition of a drop or two of HCl. If HCl has been used, add further HNO_3 and evaporate to low bulk with about 3 ml. of strong H_2SO_4 which will remove all traces of HCl and also precipitate any lead present. Dilute and filter, collecting filtrate in a 250-ml. tall beaker. The final bulk should be about 150 ml. and should contain about 4 per cent of HNO_3 and about 1 per cent of H_2SO_4. Electrolysis of the solution is carried out in a cell, containing a thick platinum wire anode and a tared platinum gauze cathode, at a voltage of 2·1 and a current of 0·5 to 0·75 amps. per square decimetre. A small quantity of urea is added to remove the oxides of nitrogen normally present or formed in nitric acid and the cathode is not completely immersed at first. After about $\frac{3}{4}$ hour the cathode is gradually lowered into the solution and when no copper is deposited on the fresh part of the gauze the estimation is complete.

When removing the assay, a beaker of water should be substituted for the trial before the current is switched off. The cathode is washed with alcohol, dried, and weighed. The residual solution should always be tested for copper with ammonia, in case the total copper has not been deposited; in this case the balance can conveniently be estimated colorimetrically.

CADMIUM, Cd; atomic weight 112·4

METALLIC CADMIUM is a ductile lustrous metal and is very similar to tin in colour. The specific gravity is 8·67. It melts at 321° C. and boils at 780° C. Cadmium oxide, CdO, varies in colour from light brown to dark brown. The chief source of cadmium in nature is the mineral greenockite, a cadmium sulphide, CdS, and it is also associated with zinc ores such as blende.

Greenockite. Cryst. system hexagonal. Colour, varies from pale to orange-yellow. Hardness 3–3·5; specific gravity 4·8–4·9 Composition: cadmium 77·7 per cent, sulphur 22·3 per cent. Occurs in Dumbarton, Scotland, and in traces with zinc blende at Thornthwaite, Cumberland. It also occurs in conjunction with calamine and other zinc ores.

Qualitative Tests

Salt used: cadmium chloride, $CdCl_2$.

1. Hydrochloric acid yields no precipitate.
2. Sulphuretted hydrogen in the presence of a little hydrochloric acid causes a yellow precipitate of cadmium sulphide to form; insoluble in ammonium sulphide, but soluble in strong nitric acid, hydrochloric and sulphuric acids:
$$CdCl_2+H_2S=CdS+2HCl$$
3. Ammonium hydroxide produces a white precipitate of cadmium hydroxide, soluble in excess:
$$CdCl_2+2NH_4OH=Cd(OH)_2+2NH_4Cl$$
4. Potassium hydroxide and sodium hydroxide form white precipitates of cadmium hydroxide; insoluble in excess (distinction from zinc):
$$CdCl_2+2NaOH=Cd(OH)_2+2NaCl$$

Cadmium is easily fusible, burning in the oxidizing flame to a brown oxide, which appears as brown fumes, forming incrustations on the charcoal. These incrustations are reddish-brown when cold, sometimes orange-yellow.

Cadmium sulphide, when heated in an open tube gives off sulphur dioxide. On the addition of HCl to the sulphide, hydrogen sulphide is evolved, which turns moistened lead acetate paper black.

Quantitative Assays

This metal, which is in appearance very similar to zinc, is almost always found in association with ores such as blende, and considerable difficulty is met with in the separation of the two metals. The presence of cadmium in spelter is especially injurious if the latter is to be used for the manufacture of zinc oxide, since quite small quantities of CdO, which has a dark yellow or brown colour, are sufficient to discolour the finished product.

Many attempts have been made to find a satisfactory method for the separation of cadmium from zinc without the use of H_2S, using precipitants such as phenyltrimethylammonium iodide or β-naphthaquinoline, but so far as is generally known at present no method supersedes that given below, variations of which are most commonly used.

Cadmium in Zinc Blende. 10 gram of the sample is weighed into a 600-ml. squat beaker and gently digested on the hot plate with aqua regia until solution is effected. The cover is then rinsed in and removed and the solution allowed to evaporate slowly to a syrupy consistency. 25 ml. of strong H_2SO_4 is cautiously added and the evaporation continued until strong fumes of SO_3 are given off, when the beaker is removed from the hot plate. When quite cold, the cake is moistened with cold water, stirred, and then boiling water added to a bulk of about 50 ml.

The solution is boiled for 10 minutes and allowed to settle for 3 or 4 hours. The lead is now removed by passing the solution through a wad of paper pulp in a funnel inserted in a pressure flask, a filter disc being placed in the bottom of the funnel prior to pouring in the pulp. The pulp and precipitate are washed with normal H_2SO_4, and the filtrate returned to the beaker. A strong current of H_2S is now passed through the solution for about 20 minutes, and the beaker is then stood aside to settle. The precipitate is collected on pulp, and the pulp and precipitate are returned to the beaker and boiled for about 10 minutes with dilute H_2SO_4 (20 per cent by volume), which will effect solution of the CdS and ZnS, any CuS present remaining insoluble. The solution is passed through pulp and washed with hot water, the filtrate returned to the beaker, and neutralized with ammonia. (It is important to add the ammonia from a beaker and not from the reagent bottle when neutralizing any solution containing H_2S, otherwise the ammonia might become contaminated and give erroneous results to another trial.) The neutral solution is evaporated down to about 50 ml. and is adjusted to approximately 2N strength with regard to the sulphuric acid by adding an appropriate amount of the strong acid. Then add 50 ml. of 10-per-cent sodium tartrate solution followed by excess of 20 ml. of a standard solution of β-naphthaquinoline in sulphuric acid, of the composition given below. Then add a few drops of dilute sulphuric acid and excess of 0·2N potassium iodide solution. Allow to stand for 20 minutes and filter through a weighed sintered glass crucible, grade G2 or G3. Wash the precipitate in the crucible with a solution containing 10 ml. of 0·2N potassium iodide, 10 ml. of the acid naphthaquinoline solution, 80 ml. of water and 2 drops of dilute sulphurous acid. Finally dry the precipitate as completely as possible by applying suction with the filter pump. Dry to constant weight at 130° C. and weigh as

$$[(C_{13}H_9N)_2\ H_2]\ (CdI_4)$$

This weight multiplied by the factor 0·1146 gives the weight of cadmium.

For greater accuracy, a volumetric titration using potassium iodate may be used. The precipitate, as obtained above, is decomposed without drying by boiling with 20-per-cent solution of 2N ammonium or sodium hydroxide. The resulting solution, which contains the cadmium, is treated successively with 60 ml. of 2N hydrochloric acid, 5 ml. of 10-per-cent potassium cyanide solution and 2 ml. of starch solution. The mixture is then titrated with 0·025M potassium iodate solution until the starch is decolorized.

$$1 \text{ ml. } 0{\cdot}025M\ KIO_3 \equiv 0{\cdot}001405 \text{ gram Cd}$$

The above methods permit the separation of cadmium from relatively large quantities of zinc, iron, chromium, aluminium, cobalt, manganese and magnesium. If ammonium oxalate is added in addition to the sodium tartrate, or a larger amount of sodium tartrate is used, then the determination can be carried out in the presence of antimony and tin.

Standard solution required:

1. β-naphthaquinoline: dissolve 2·5 gram β-naphthaquinoline in 100 ml. of 0·5N H_2SO_4.
2. 2N solution of potassium iodide.
3. 0·025M solution of potassium iodate.

ARSENIC (Arsenicum), As; atomic weight 74·96

ARSENIC is trivalent and pentavalent. In dry air arsenic is steel-grey in colour, and possesses a good lustre, but as usually found is of dull appearance due to slight oxidation. Arsenic has a unique position amongst the elements being a half-way house as it were between the non-metals and metals.

Native Arsenic is frequently found in conjunction with lead and silver ores. It occurs in nature in various forms, sometimes massive, at others granular, stalactitic, kidney shaped and columnar. A brittle mineral. Hardness 3·5; specific gravity 5·93. Most of the arsenic of commerce is derived from mispickel, an arsenical iron pyrite, which will be described under iron-bearing minerals. Two other arsenic minerals are the yellow sulphate, *Orpiment*, As_2S_3, and the red sulphide, *Realgar*, As_2S_2.

Qualitative Tests

Arsenious oxide, As_2O_3, dissolved in hydrochloric acid.

1. Sulphuretted hydrogen in the presence of HCl causes a yellow precipitate of arsenious sulphide to form; soluble in ammonium sulphide, forming ammonium thioarsenite $(NH_4)_3AsS_3$; insoluble in boiling hydrochloric acid (distinction from the sulphides of antimony and tin), soluble in solution of ammonium carbonate (distinction from antimony and tin):

$$2AsCl_3+3H_2S=As_2S_3+6HCl$$

2. The hydroxides of potassium, sodium and ammonium yield no precipitates (distinction from antimony).
3. A strip of bright copper boiled in a solution of arsenious oxide in hydrochloric acid is covered with a grey deposit of cupric arsenide. On drying the copper carefully and heating in a wide tube, a crystalline sublimate of arsenious oxide will be obtained. Under the microscope the crystals of the sublimate appear mostly as octahedra:

$$3Cu+2AsCl_3=3CuCl_2+2As$$

Tests for arsenites

1. Copper sulphate added to a neutral solution of sodium arsenite forms a bright yellowish-green precipitate of cupric hydrogen arsenite, $CuHAsO_3$ (Scheele's green):

$$Na_2HAsO_3+CuSO_4=CuHAsO_3+Na_2SO_4$$

2. Silver nitrate added to a neutral solution of an arsenite forms a yellow precipitate of silver arsenite, Ag_3AsO_3, that is readily soluble in nitric acid.

Marsh's Test

Hydrogen is generated from arsenic-free granulated zinc and pure dilute sulphuric acid, in a flask about 300 ml. capacity. The flask is closed by a rubber stopper with two holes. Through one passes a thistle funnel reaching to nearly the bottom of the flask, whilst through the second hole passes a glass tube leading to a drying tube containing calcium chloride. To the other end of the tube containing calcium chloride is fitted a narrow glass tube drawn out to a small jet at the far end. Hydrogen is generated by pouring the dilute sulphuric acid on to the arsenic-free zinc and is dried during its passage through the calcium chloride. Three or four minutes should elapse before applying a light to the jet at the end of the delivery tube to make sure that all the air has been expelled from the flask. Then pour half-a-dozen drops of the arsenical solution down the thistle funnel, when arsenic hydride will be produced. If a porcelain crucible cover is held by crucible tongs in the burning hydrogen jet, a brown spot of arsenic will be deposited on the cold surface of the cover. These spots are soluble in a solution of chlorinated lime:

(i) $As_4O_6 + 12H = As_4 + 6H_2O$
(ii) $As_4 + 12H = 4AsH_3$ (arsenic hydride)

Fleitmann's Test.

Place some arsenic-free granulated zinc in a flask and add a concentrated solution of potassium or sodium hydroxide, heating nearly to the boiling point:

$$Zn + 2NaOH = H_2 + Na_2ZnO_2$$

When the hydrogen is coming off briskly add a few drops of arsenical solution, and then quickly spread over the mouth of the flask a filter paper cap moistened with a solution of silver nitrate. Heat the flask, taking care that the liquid in the flask does not spurt up on to the cap. The arsenical compound is reduced to arsenic, which unites with the hydrogen, forming, as in the former test, arsenic hydride, which interacts with the silver nitrate to produce a purplish-black stain of silver:

$$AsH_3 + 3H_2O + 6AgNO_3 = H_3AsO_3 + 6HNO_3 + 6Ag$$

This is a very useful test since it enables the worker to recognize arsenic in the presence of antimony, due to the fact that in the reduction, carried out in an alkaline solution, antimony hydride is not produced.

Arsenical minerals give, in the oxidizing flame, on charcoal, an orange-yellow incrustation, indicating arsenious sulphide, with such minerals as realgar, orpiment, arsenical pyrites and cobalt-glance. In a closed tube bright metallic mirrors are produced and in the open tube white sublimates and a garlic-like smell.

Quantitative Assays

This mineral is often purchased as " crude white arsenic " and can be most readily estimated by titration with standard iodine solution. A suitable quantity is weighed into a 450-ml. conical beaker, and the arsenic dissolved in caustic-soda solution. A slight excess of HCl is added, and then a large excess of solid sodium bicarbonate. The iodine solution is titrated into the cold solution, using starch as indicator, until the blue colour persists.

Another method, very suitable for the estimation of arsenic in ores, is based on the formation of uranyl arsenate from arsenious acid and uranium acetate, the excess of the latter being shown by the brown coloration of drops of potassium ferrocyanide solution. The arsenic is separated from antimony in the form of sulphide by passing H_2S gas through a strongly acid solution of the Group IIA metals, the arsenic being precipitated and the antimony remaining in solution. The precipitate is redissolved in ammonium-sulphide solution, boiled to expel excess ammonia and H_2S, and then a few ml. of HNO_3 is added. Boiling is continued until the arsenic has redissolved and the sulphur oxidized. The bulk should now be not more than 50 ml. The solution is neutralized with ammonia and 5 ml. of sodium-acetate solution and titrated boiling with standard uranium-acetate solution, using drops of potassium ferrocyanide solution as outside indicator.

Solutions required:

Uranium Acetate Solution. 34 gram of A.R. grade uranium acetate is dissolved in water, and 25 ml. glacial acetic acid added. The solution is diluted to 1 litre. 1 ml. will be equivalent to 5 mg. of arsenic.

Indicator. 10-per-cent potassium ferrocyanide solution.

Sodium Acetate. 10 gram in 50 ml. acetic acid and 40 ml. distilled water, made up to 250 ml.

ANTIMONY, Sb (*Stibium*); atomic weight 121·76

THIS element is chiefly found in the trivalent and pentavalent forms. It is a bluish-white, but very brittle, lustrous metal, melting at 630° C. and boiling at 1440° C. It has a specific gravity of 6·5–6·7. Antimony enters into many alloys: such as britannia metal, consisting of tin 90·62 per cent, antimony 7·81 per cent, copper 1·46 per cent; white metal, tin 82 per cent, antimony 12 per cent, copper 6 per cent; also several lead alloys such as type metal, lead 70 per cent, antimony 18 per cent, tin 10 per cent; bearing metal, lead 84 per cent, antimony 16 per cent; also lead 60 per cent, antimony 20 per cent, and tin 20 per cent. Other alloys of antimony, lead and tin are used industrially.

The only mineral of importance is *Stibnite* or *Grey Antimony*, Sb_2S_3. Cryst. system rhombic, occurring in rhombic prisms. Colour, lead-grey; lustre metallic; fracture subconchoidal. Hardness 2; specific gravity 4·5–4·6. Composition: antimony 71·6 per cent, sulphur 28·2 per cent. Found at Carrock Fell and Robinhood mine, Bassenthwaite, Cumberland; near Padstow and Tintagel in Cornwall. It is also found in various parts of the world such as Hungary, Spain, Borneo and the U.S.A.

There are also several sulphides of lead and antimony such as *Jamesonite*, $Pb_2Sb_2S_5$, a fibrous and acicular mineral; also *Red Antimony* or *Kermesite*, $Sb_2O_3.2Sb_2S_3$, an oxysulphide, and two rare minerals: *Valentinite*, Sb_2O_3, and *Senarmontite*, Sb_2O_3, but these minerals are of little importance except as specimens, the ore stibnite or antimonite being the chief source from which the metal and the white pigment, antimony white, or timonox, are produced.

Qualitative Tests

Use a solution of antimonious chloride, $SbCl_3$, in hydrochloric acid.

1. On the addition of HCl a white precipitate of antimony oxychloride, SbOCl, is likely to be formed, but on the addition of a few drops of strong hydrochloric acid, and warming the liquid, this will dissolve. This reaction is reversible:

$$SbCl_3+H_2O \rightleftharpoons SbOCl+2HCl$$

2. In the presence of hydrochloric acid, sulphuretted hydrogen gives an orange precipitate of antimonious sulphide; soluble in ammonium sulphide, forming ammonium thioantimonite $(NH_4)_3Sb_3$; also soluble in strong boiling hydrochloric acid, but insoluble in cold dilute acid.
3. Ammonium sulphide gives an orange-red precipitate of antimony trisulphide in the case of solutions containing trivalent antimony only.
4. Potassium and sodium hydroxides form a white precipitate of antimonious oxide; soluble in excess. Ammonium hydroxide also yields a similar precipitate.:

$$2SbCl_3+6NH_4OH=Sb_2O_3+6NH_4Cl+3H_2O$$

5. Marsh's test, as described under Arsenic, gives stains of antimony on a porcelain crucible lid, which are not removed when treated with chlorinated lime solution.
6. If a strip of bright copper foil is boiled in a solution containing antimony, and acidulated with hydrochloric acid a black coating is produced on the copper. This, when removed and carefully dried between filter paper and then heated in a dry tube, forms an amorphous sublimate of Sb_2O_3. If this sublimate is then dissolved in a few drops of acid-potassium tartrate, and treated with H_2S, an orange precipitate of antimonious sulphide will form. On charcoal, with the oxidizing flame, antimony forms a red incrustation.

Quantitative Assay

The following method is perhaps the most accurate for all general purposes.

0·5–5 gram of the finely crushed ore is dissolved in HCl containing a little $KClO_3$. About 2 gram of tartaric acid is added and the solution is filtered to remove the insoluble matter, the filtrate and washings being collected in a large (600 ml.) conical flask. The solution is diluted to about 400 ml. and H_2S passed until the solution is saturated with the gas. The precipitate, after settling, is collected by filtering the solution through a wad of paper pulp in a funnel, at the bottom of which has been placed a filter disc; a moderate suction being employed. The pulp and precipitate are returned to the beaker, together with about 50 ml. hot water and 10 ml. of 10-per-cent sodium-sulphide solution, and the whole brought to the boil to effect solution of the antimony sulphide and any tin or arsenic present. The solution is again passed through pulp and washed well with hot water, the filtrate being returned to the beaker.

The filtrate is now made acid with HCl and brought to the boil, bromine water or $KClO_3$ being added to complete solution of the antimony and the sulphur. Boiling is continued until the solution is quite clear and the bulk not more than 100 ml. Strong HCl is now added until the bulk is increased to about 250–300 ml., and then H_2S is passed for an hour. Any arsenic present will be precipitated, while the antimony will be held up by the strong acid. The former is removed by filtering through pulp, the precipitate being washed with a solution containing two parts of HCl to one part of water. The filtrate is again transferred to the beaker, and after the addition of 2 gram of tartaric acid, the bulk of the acid is neutralized with ammonia (from a beaker, not a bottle) and H_2S is again passed to complete the precipitation of the antimony.

After settling, the precipitate is collected on a close filter paper, well washed with hot water and H_2S water, and then washed into a 400-ml. Erlenmayer flask (preferably Pyrex), using as little water as possible. The paper is cleaned with a little sodium-sulphide solution, the washings being collected in the flask.

About 5 gram of sodium sulphate is added, together with about 5 ml. strong H_2SO_4, and the contents are now boiled over a naked flame until all the water and most of the acid is removed and the sodium sulphate is molten. (The flask must be held in a pair of tongs and the contents constantly rotated to avoid breakage.) When quite cold, the contents are taken up with 100 ml. of hot water, boiled for about 15 minutes to expel SO_2 fumes, and allowed to cool again. To the cold flask 10 ml. strong HCl is added, and the antimony is titrated with decinormal potassium-permanganate solution (1 ml.=6·02 mg.).

For the estimation of antimony in lead or solder alloys, a suitable portion of the drillings can be treated direct by fusing with H_2SO_4 and sodium sulphate as above. By this method a determination can be completed in well under an hour, with very accurate results.

TIN, Sn (*Stannum*); atomic weight 118·70

TIN is a metal greyish-white in colour, very lustrous, ductile and soft. Tin melts at 232° C., boils at 2270° C., and is easily oxidized when heated in the air. Specific gravity (tetragonal) 7·20. The alloys of tin have already been mentioned under antimony, such as britannia metal, which contains approximately 90·62 per cent, white metal 52–82 per cent, and ashberry alloy 77·80 per cent Sn and 19·4 per cent Sb. There are two important ores of tin, *Cassiterite*, SnO_2, and *Stannine* or *Tin-pyrites*, $2Cu_2SnS_2+2(FeZn)S.SnS_2$.

Cassiterite, otherwise called *Tin-stone*. Cryst. system tetragonal. Usual form tetragonal prisms, the crystals are frequently twinned. It is also found massive and granular. Colour, black-brown, sometimes yellowish. Fracture subconchoidal or uneven. Hardness 6–7; specific gravity 6·4–7·2. Composition (stannic oxide): tin 78·38 per cent, oxygen 21·62 per cent. Manganese and iron often occur in small amounts as impurities. Found in many Cornish mines and formerly was one of the leading industries there. Most of the old mines are now closed. It also occurs in Malaya, Australia, Bolivia, Burma, Siam and Nigeria.

Stannine. This is a complex ore. Cryst. system cubic-tetrahedral and usually occurs massive or granular. Colour, steel-grey or iron-black. When, however, copper pyrites is present, the mineral has a yellowish appearance; lustre metallic; fracture uneven. Hardness 4; specific gravity 4·3–4·5; consists of sulphides of tin, iron and copper: tin 27 per cent, iron 13 per cent, copper 30 per cent, sulphur 30 per cent. Zinc is also often present. Found in many old Cornish mines.

Qualitative Tests

Stannous Salts.

For stannous salts a solution of stannous chloride, $SnCl_2$, should be used.

1. Hydrochloric acid yields no precipitate.
2. Sulphuretted hydrogen in the presence of HCl causes a brownish precipitate of stannous sulphide to form: soluble in ammonium sulphide and boiling hydrochloric acid:

$$SnCl_2+H_2S=SnS+2HCl$$

3. Potassium and sodium hydroxide and ammonium hydroxide cause a white precipitate of stannous hydroxide to form.

$$SnCl_2+2KOH=Sn(OH)_2+2KCl$$

4. A solution of mercuric chloride causes a white precipitate of mercurous chloride to form:

$$SnCl_2+2HgCl_2=2HgCl+SnCl_4$$

If the precipitate is boiled with excess of stannous chloride, a grey precipitate of mercury is formed:

$$SnCl_2+2HgCl=2Hg+SnCl_4$$

Stannic Salts

Use a solution of stannic chloride, $SnCl_4$.

1. Sulphuretted hydrogen causes a yellow precipitate of stannic sulphide to form: soluble in ammonium sulphide, forming ammonium thiostannate $(NH_4)_2SnS_3$.

$$SnCl_4+2H_2S=SnS_2+4HCl$$

2. The hydroxides of potassium, sodium and ammonium form a white precipitate of stannic hydroxide, $Sn(OH)_4$; soluble in excess.
3. If a piece of iron wire be placed in a solution containing antimony and tin together with a little HCl a black precipitate of antimony will be formed, and the tin will be reduced to the stannous condition. The latter can then be detected by adding a solution of

mercuric chloride, when a white precipitate of mercurous chloride will form. This is a useful test for separating and detecting antimony and tin:

$$2HgCl_2+SnCl_2=2HgCl+SnCl_4$$

If stannous compounds are mixed with equal parts of sodium carbonate and potassium cyanide and heated on charcoal by the reducing flame of a blowpipe, a granule of metallic tin will result. Having dissolved the granule in hydrochloric acid, filter to remove any specks of charcoal, and then apply some of the tests described above.

When stannic oxide is heated in a glass tube with potassium cyanide it is reduced.

Quantitative Assay

0·5–1 gram of the mineral is weighed into a 450-ml. conical beaker and dissolved in about 30 ml. concentrated HCl with the aid of a little $KClO_3$. When completely dissolved, the solution is boiled to expel chlorine fumes and made up to about 300 ml. with distilled water. Two iron nails or strips of wire of about $\frac{1}{8}$ inch diameter are carefully cleaned and inserted in the beaker and the reduction allowed to proceed for an hour. The solution is then filtered through a No. 4 Whatman paper into a 600-ml. flask in which a coil of nickel attached to a thin glass rod has previously been placed. After boiling steadily for an hour, the flask is cooled quickly, a piece of marble inserted, and a cork and funnel (the latter fitted with a bunsen valve and filled with soda-ash solution) fitted in the neck. When quite cold, the nickel is rinsed out and the solution immediately titrated with N/10 iodine, using starch paste as indicator.

Where stannic ores are to be tested, it is sometimes necessary to reduce the charge in a porcelain boat in a combustion tube, by passing hydrogen or coal gas over at red heat before dissolving. Alternatively the charge may be weighed into a nickel crucible and fused with about 6 gram of sodium peroxide to effect solution.

GOLD, Au (*Aurum*); atomic weight 197·2

GOLD is both monovalent and trivalent. It is a very ductile metal, very lustrous, and yellow in colour. According to its state of precipitation it varies in colour. In the usual metallic state it is yellow, when in powder form, brown, but in the colloidal state, red or blue.

The melting point is 1063° C., boiling point 2500° C., and specific gravity 19·3.

Gold is soluble in aqua regia, but does not dissolve in hydrochloric, nitric or sulphuric acids alone. Gold does not oxidize in the air even when strongly heated. It is found as native gold. Cryst. system cubic. Usually occurs as grains or scales in sands of an alluvial character, and frequently associated with various precious stones, such as ruby, sapphire, topaz and garnet and other highly coloured specimens of oxides of aluminium, as well as in quartz veins of metamorphic origin. Hardness 2·5–3; specific gravity 12–20, the various values for specific gravity being due to other metals with which the gold may be associated, such as silver, copper, iron, rhodium or palladium. Gold in the British Isles has been found in small amounts in Carmarthenshire, near Dolgelly, in Merioneth, in the stream workings in Cornwall, at Goldscope and Brandley mines, Cumberland, Leadhills in Lanark, Scotland, and several other places, such as the Wicklow Mountains. It also occurs in Thibet, China, Japan, Borneo, Abyssinia, South Africa, Australia, India, and in several republican countries of South America and other parts of the world.

Qualitative Tests

Use a solution of auric chloride, $AuCl_3$.

1. Sulphuretted hydrogen in the presence of HCl causes black auric sulphide to form when cold, but should the solution be hot then aurous sulphide, Au_2S, is produced. Both are soluble in mixed nitric and hydrochloric acids, in yellow ammonium sulphide; and in solutions of potassium and sodium sulphides:

$$2AuCl_3+3H_2S=Au_2S_3+6HCl$$

2. Colloidal gold is precipitated from an acidulated solution by boiling with oxalic acid or any reducing agent. The colloidal gold may exhibit various colours, e.g. blue, green, brown and purple.
3. Stannous chloride, $SnCl_2$, causes a purple or brownish-purple precipitate to form, known as " purple of Cassius," which consists of a mixture of oxides of gold and tin.
4. Metals such as copper, zinc and iron, as well as several other metals, especially when in the powder form, such as zinc dust, form precipitates of metallic gold in a very fine colloidal state.

When heated on charcoal all compounds of gold are reduced, yielding golden particles, readily soluble in aqua regia.

If borax, $Na_2B_4O_7.10H_2O$, is first partly dehydrated by heating in the blowpipe flame, then dipped in a weak solution of auric chloride or other gold salt, and fused into a bead, various colours appear as the bead is heated; first ruby-red, then blue, and later, after more heating, greenish-blue and finally colourless. This is a characteristic test for gold.

Quantitative Assay

(See Part III, page 99)

PLATINUM, Pt; atomic weight 195·2

THIS element is divalent and tetravalent. Metallic platinum is highly lustrous and ductile, and steel-grey in colour. Melting point is approximately 1750° C., and specific gravity 21·4. There are two other varieties of platinum: spongy platinum, which has a dull grey colour, and a precipitated variety, platinum black. Platinum is not dissolved by hydrochloric acid, sulphuric acid or nitric acid, but is soluble in hot aqua regia. Platinic oxide, PtO_2, is a black powder, and platinous oxide, PtO, is dark violet in colour. Platinum occurs as native platinum. Cryst. system cubic, and usually is found as grains or in irregularly-shaped lumps. Hardness 4–4·5; specific gravity 16–19. Other elements found with platinum are gold, iron, copper and a number of rare elements, such as iridium, osmium, rhodium and palladium. Deposits occur in Brazil, in the Urals, Borneo and California.

Qualitative Tests

A solution of platinic chloride, $PtCl_4$, is used.

1. Sulphuretted hydrogen, in the presence of hydrochloric acid, causes a brown precipitate of platinic sulphide, PtS_2, to form. The precipitate forms slowly and is dissolved by yellow ammonium sulphide:

$$PtCl_4+2H_2S=PtS_2+4HCl$$

2. Potassium chloride in the presence of HCl, with the addition of a little alcohol, gives a yellow crystalline precipitate of potassium platinic chloride, PtK_2Cl_6:

$$2KCl+H_2PtCl_6=K_2PtCl_6+2HCl$$

3. Zinc dust and finely powdered iron, as well as several other metals, decompose platinic salts, causing a deposit of the metal.

Platinum salts are reduced to metal when heated on charcoal with sodium carbonate by the reducing flame of a blowpipe. Dehydrated borax beads which have been dipped or moistened in a solution of platinic salt, and then fused, are coloured brown.

IRON (Ferrum), Fe; atomic weight 55·84

THE ores of iron are present in two forms: the ferrous condition or divalent ores, and the ferric condition or trivalent ores. Iron also exists in the hexavalent state as somewhat unstable ferrates. When pure, iron is whitish-grey, specific gravity being 7·8, melting at approximately 1550° C. Iron is highly magnetic. There are several important ores of iron of which the following is a brief list.

Magnetic Iron Ore, or *Magnetite*, is the Swedish ore, Fe_3O_4. Cryst. form cubic, commonly found octahedral or rhombic dodecahedral. Colour, black or greyish-black. Fracture subconchoidal. Hardness 5·5–6·5; specific gravity 4·9–5·3. Strongly magnetic. Average composition: ferric oxide 69 per cent, ferrous oxide 31 per cent. In some cases a portion of the iron is replaced by titanium.

Hæmatite or *Kidney Ore*. Cryst. system rhombohedral. Colour, iron-black or steel-grey, but in thin sections it has a blood-red colour, and when found " earthy " is also red in colour. Lustre metallic. Fracture uneven or subconchoidal. Hardness 5·5–6·5; specific gravity 4·5–5·2. Composition: ferric oxide, Fe_2O_3, 100 per cent; or iron 70 per cent, oxygen 30 per cent.

Another form of ferric oxide is *Specular Iron Ore*, so called from the fact that the crystalline structure is highly lustrous, in other words it is crystallized hæmatite. Large quantities are found in Russia.

Limonite or *Brown Hæmatite*, $2Fe_2O_3.3H_2O$. Usually occurs in large spheroidal surfaces or is stalactitic in form. Has a dull silky appearance. Colour, brown or yellowish-brown. Hardness 5–5·5; specific gravity 3·6–4·0. Much of the French iron is made from this ore. Bog iron ore is a limonite ore of a loose, porous nature, found in low-lying and damp situations or swampy ground.

Clay Ironstone is an impure iron carbonate of an argillaceous nature, occurring in beds, often in conjunction with the Coal Measures, and in other clay deposits such as the Middle Lias.

Chalybite or *Spathic Iron Ore*. Cryst. system hexagonal. Usual form rhombohedral, the crystal faces being frequently curved. Occurs most frequently massive, but also found granular. Colour varies from light yellow, through various shades of brown, from buff to brownish-red and brownish-black. Fracture uneven. Hardness

3·5–4·5; specific gravity 3·7–3·9. A carbonate of iron, $FeCO_3$: iron 61 per cent, carbon dioxide 38 per cent. Small amounts of lime, manganese and magnesium, usually less than 1 per cent.

Iron Pyrites. Cryst. system cubic. Gives off sparks when sharply struck. A yellow lustrous mineral which has been largely employed as a source of sulphur. Lustre metallic to highly lustrous. Fracture uneven or conchoidal. Hardness 6–6·5; specific gravity 4·8–5·1. Composition: a sulphide of iron, FeS_2: iron 47 per cent, sulphur 53 per cent. *Marcasite*, has the same composition, but crystallizes in the rhombic system.

Gothite. Cryst. system rhombic. Found massive, stalactitic-kidney-shaped and fibrous. Colour, yellow, yellowish-red and dark-brown, turning black. Hardness 5–5·5; specific gravity 4–4·3. Composition: hydrated ferric oxide, $Fe_2O_3.H_2O$: ferric oxide 85 per cent, water 10–11 per cent. The balance is frequently made up of silica and manganese.

Mispickel, or arsenical iron pyrites, has already been mentioned under arsenic. The cryst. system is rhombic, the usual form being rhombic prisms. Colour, tin-white, sometimes steel-grey. Lustre metallic. Fracture uneven. Hardness 5·5–6; specific gravity 6·2–6·3. Composition, $FeAs.S$: iron 30·36 per cent, arsenic 40–45 per cent, sulphur 18–21 per cent. Occasionally cobalt is also present, as found at the old cobalt mine, Scar Crag, Cumberland, in quantities from 0·5 per cent to 4·0 per cent.

Pyrrhotine. A magnetic pyrites. Cryst. system hexagonal. Colour, usually reddish-brown. Fracture uneven or semiconchoidal. Hardness 3·5–4·5; specific gravity 4·4–4·65. Composition, iron sulphide, Fe_6S_7: iron 60·5 per cent, sulphur 39·5 per cent. Often contains small amounts of nickel varying from 0·4 per cent to 0·85 per cent.

Lievrite Iron and *Calcium Silicate.* Cryst. system rhombic, usually found as rhombic prisms. Colour, dark brown to black. Fracture uneven. Hardness 5·5–6; specific gravity 3·8–4·0. Composition, an iron and calcium silicate, $CaFe_2Fe(OH)(SiO_4)_2$: iron oxide 50–55 per cent, lime 14 per cent, silica 29 per cent.

Franklinite. This ore, which will be referred to under zinc, contains ferric oxide 54–60 per cent.

Melanterite or *Copperas.* Cryst. system monoclinic. Colour, green to yellowish-brown, sometimes found nearly white with a greenish cast. Fracture conchoidal. Hardness 2; specific gravity 1·82–1·83. A hydrated sulphate of iron, $FeSO_4.7H_2O$: iron 25 per cent, sulphates 29 per cent, water 45 per cent.

Vivianite. Cryst. system monoclinic, commonly found as oblique rhombic prisms; also occurs kidney-shaped and encrusting. Colour, blue, greenish-blue or green. Lustre vitreous, sometimes pearly. Hardness 1·5–2; specific gravity 2·64–2·66. A hydrated iron phosphate, $Fe_3(PO_4)_2 8H_2O$: ferrous oxide 42–44 per cent, phosphoric acid 26–30 per cent, water 27–28 per cent. Ferric oxide is also sometimes present.

Qualitative Tests

Salt used (ferrous iron), ferrous sulphate, $FeSO_4.7H_2O$.

1. Sulphuretted hydrogen in the presence of hydrochloric acid gives no reaction with ferrous salts.
2. Ammonium sulphide causes a black precipitate of ferrous sulphide to form. The solution to which the reagent is added should be neutral or alkaline. It is easily soluble in dilute hydrochloric acid, but is insoluble in acetic acid:

$$FeSO_4+(NH_4)_2S=FeS+(NH_4)_2SO_4$$

3. Potassium and sodium hydroxides, also ammonia, cause a greenish-brown precipitate of ferrous hydroxide, $Fe(OH)_2$, to form. The precipitate turns brown on the top very soon due to oxidation, being converted to ferric hydroxide:

$$FeSO_4+2NH_4OH=Fe(OH)_2+(NH_4)_2SO_4$$

4. Potassium ferrocyanide in neutral or slightly acid solutions gives a whitish precipitate, quickly changing to pale-blue potassium-ferrous-ferrocyanide, which is decomposed by alkalies:

$$FeSO_4+K_4Fe(CN)_6=K_2Fe(Fe(CN)_6)+K_2SO_4$$

5. Potassium ferricyanide causes a deep-blue precipitate (Turnbull's blue) to form, which is decomposed by alkalies, but the blue is restored on the addition of hydrochloric acid:

$$3FeSO_4+2K_3Fe(CN)_6=Fe_3(Fe(CN)_6)_2+3K_2SO_4$$

6. Potassium thiocyanate gives no precipitate.

Ferric Compounds

Salt used: ferric chloride, $FeCl_2$.

1. Ammonium sulphide causes a black precipitate to form. It is insoluble in acetic acid.:

$$2FeCl_2+3(NH_4)_2S=2FeS+S+6NH_4Cl$$

2. Potassium and sodium hydroxides, also ammonia, yield a brown

precipitate with ferric compounds of ferric hydroxide, $Fe(OH)_3$. In the case of ferrous hydroxide, this is slightly soluble in excess, whereas the ferric hydroxide is insoluble, therefore before adding the alkali it is well to warm the solution with a few drops of nitric acid to make sure that all the iron present is in the ferric state. Organic acids, such as citric or tartaric, and their salts, prevent this reaction taking place, so, should such admixture be suspected, the solution must first be evaporated to dryness, the residue heated to redness, and then dissolved in dilute hydrochloric acid plus a drop or two of nitric acid, and heated. Finally add distilled water and then the alkali and boil, when the ferric hydroxide will be completely precipitated:

$$FeCl_3+3NH_4OH=Fe(OH)_3+3NH_4Cl$$

3. Potassium ferrocyanide gives a deep-blue precipitate (prussian blue) of ferric ferrocyanide, which is decomposed by alkalies:

$$4FeCl_3+3K_4Fe(CN)_6=Fe_4(Fe(CN)_6)_3+12KCl$$

4. Potassium ferricyanide causes a brown solution to form with ferric salts, but no precipitate.
5. Potassium thiocyanate causes a deep blood-red coloration with ferric compounds, due to ferric sulphocyanide:

$$FeCl_2+3KSCN=Fe(SCN)_3+3KCl$$

With the borax bead a brownish bead is produced in the oxidizing flame, while in the reducing flame the bead is bottle-green. With microcosmic salt the oxidizing flame gives a yellow to reddish-green bead when hot, and, when cold, a colourless to yellow or brown bead. In the reducing flame the bead is yellow to reddish-green when hot, colourless to reddish when cold.

Quantitative Assays

Iron or manganese ores can usually be dissolved by HCl with the aid of stannous chloride. From 1 to 2 gram of the mineral is weighed into a 600-ml. beaker and about 30 ml. of strong HCl is added. After gently stewing on the hot plate for about 10 minutes, a few millilitres of stannous chloride are added. (It is preferable to make up the latter from metallic tin and HCl rather than from the solid salt.) Precipitate Group II metals with H_2S and filter. Oxidize the solution by the addition of a few drops of concentrated HNO_3, and add NH_4Cl and NH_4OH till alkaline. Filter, wash the precipitate with hot water and dissolve in warm HCl. Add dilute $SnCl_2$ solution drop by drop until the solution is colourless and cool. The solution is now made up to about 300 ml. with cold distilled water, 10 ml. of saturated mercuric-chloride solution added, and stirred vigorously. Standard potassium-bichromate solution is now run in from a burette, and from time to time a drop of the solution is brought in contact with drops of dilute potassium-ferricyanide solution on a porcelain plate. Alternatively the titration may be carried out using sodium diphenylamine sulphonate as internal indicator.

In the case of ores containing copper or zinc it is necessary to dissolve the material in aqua regia, add ammonium chloride and then excess ammonia, boil for 5 minutes, allow to settle, and filter through a No. 4 or 31 Whatman paper. Wash well with hot water and ammonia (redissolve and reprecipitate if necessary), dissolve in HCl, add a slight excess of stannous chloride and proceed as above.

An alternative method for the determination of iron is by titration with potassium permanganate. In this case no external indicator is necessary, the pink colour of the permanganate in slight excess indicating the end-point. Where permanganate is used, however, no HCl must be present, so that if HCl has been used to effect solution it must be removed by evaporating the solution with strong H_2SO_4 until fumes of sulphur trioxide are freely evolved A very useful method for iron ores is to fuse the sample in a platinum crucible with $KHSO_4$.

After solution is effected by either of the above methods, the iron is reduced to the ferrous state by the addition of granulated zinc. The reduction is complete when a drop of the solution gives no coloration when mixed with a drop of potassium or ammonium-thiocyanate solution on a porcelain plate, the slightest trace of ferric iron present giving a characteristic blood-red coloration. The excess zinc is removed by filtering the solution rapidly through glass wool, a piece of marble is inserted, and the solution at once titrated with $KMNO_4$. It is essential to have a good excess of H_2SO_4 present, so that more should be added after the removal of the zinc.

COLORIMETRIC ESTIMATION OF IRON

This method is used for extremely small quantities of iron, such as exist in samples of magnesia, zinc oxide, or refined spelter, and is based on the blood-red coloration imparted to ferric solutions by the addition of ammonium or potassium thiocyanate. The procedure is as follows:

A suitable quantity of the material under examination is dissolved in HCl or aqua regia, and taken to fuming with H_2SO_4. It is best in the case of zinc oxide or spelter to evaporate almost to dryness before adding the (concentrated) H_2SO_4; otherwise considerable loss will be caused by spitting, besides the risk of breaking the beaker. After strongly fuming, the beaker is allowed to cool, cold water added to soften the cake and then about 200 ml. of boiling water. The solution is boiled for about 10 minutes and allowed to settle for at least 3 hours, after which the lead is filtered off and the Fe precipitated with ammonia. The iron, after settling, is collected on an open paper, redissolved in HCl, and again precipitated with ammonia and filtered.

The precipitate is dissolved in HCl, transferred to a small beaker, and evaporated to fuming with a few drops of HNO_3 and H_2SO_4. When cool, it is taken up with a few millilitres of water and transferred to a Nessler tube. 2 ml. of saturated KCNS is added and the solution is diluted to the mark with distilled water. A similar tube is placed alongside the sample, containing the same quantity of KCNS and water, and standard ferric-sulphate solution is added from a burette to the latter until the colours of the two tubes match in density.

Standard Ferric Sulphate. 0·35 gram of A.R. ferrous ammonium sulphate is dissolved in water, oxidized with a few drops of HNO_3, and made up to 2·5 litres. 1 ml. of the solution will contain 0·02 mg. of Fe.

ALUMINIUM, Al; atomic weight 27·1

ALUMINIUM is present in practically every type of soil and in many rocks which make up the earth's surface. Large quantities of aluminium are obtained from the minerals bauxite and cryolite. It is a white metal; specific gravity 2·853; melting point 657° C; boiling point 1800° C. It is easily dissolved by hydrochloric acid with the evolution of hydrogen. It is very ductile and can be rolled out into thin sheets, and is strongly resistant to air and moisture. In the form of powder it enters into the composition of many types of metallic paints, and is also used today in many alloys, in conjunction with the metals iron, copper, beryllium and magnesium. The alloy of aluminium 90 per cent and magnesium 10 per cent is lighter than pure aluminium itself. Of the various minerals in which aluminium occurs the following are some of the most important:

Bauxite. A ferruginous aluminium hydroxide. Colour, white, red or brown, and usually found massive. Composition: an aluminium-iron-hydroxide $(Al_2O_3Fe_2O_3)H_2O$.

Cryolite. Cryst. system triclinic. Found in various colours: white, yellowish-white or pale yellow, reddish-white and even very dark brownish-black. Lustre vitreous. Hardness 2·5; specific gravity 2·9–3·0. A sodium-aluminium fluoride, $6NaF.Al_2F_6$: sodium 32·8 per cent, aluminium 13 per cent, fluorine 54·2 per cent.

Corundum. Cryst. system hexagonal, generally found in six-sided pyramids or massive, but also found in the granular state. Colour of common corundum, reddish or greenish, also found greyish and occasionally colourless. Several precious stones consist of corundum, such as the ruby, sapphire and amethyst, the value of these stones depending on their clearness, depth of colour, transparency and freedom from flaws. The fracture is usually conchoidal. Hardness 9; specific gravity 3·9–4·1. Composition, alumina, Al_2O_3: aluminium 53·4 per cent, oxygen 46·6 per cent. On being rubbed with a cloth becomes electrified. *Emery* is an impure variety of corundum.

Spinel. Cryst. system cubic. Colour, various: red, brownish-red, brown, green, blue and black. Lustre vitreous. Hardness 8; specific gravity 3·5–3·6. Composition: aluminium and magnesium oxides, $MgO.Al_2O_3$. Most specimens contain small amounts to traces of iron, calcium and silica. A violet variety is known as almandine ruby.

Alumstone. Cryst. system hexagonal. Occurs massive, fibrous or granular. Colour, white, greyish-white or reddish-white. Lustre dull or vitreous. Hardness 3·5–4; specific gravity 2·59–2·75. Composition, hydrated aluminium sulphate, $K_2SO_4.3Al(SO_4)_3.6H_2O$: alumina 37·13 per cent, potash 11·34 per cent, sulphuric anhydride 38·53 per cent, water 13 per cent. When very massive, considerable amounts of silica may be present.

Alunogene. Cryst. system monoclinic. Frequently found in a fibrous form. Colour, white, yellowish-white or pale yellow, or reddish-white to light red. Lustre vitreous. Hardness 1·5–2·0; specific gravity 1·6–1·8. Composition, hydrated aluminium sulphate $Al_2(SO_4)_3.18H_2O$: alumina 15·4 per cent, sulphuric anhydride 36 per cent, water 48·6 per cent.

Chrysoberyl. Cryst. system rhombic. Occurs mostly in modified rectangular prisms. Colour, grass-green or yellowish-green, sometimes nearly white but having a green tinge. Lustre vitreous. Hardness 8·5; specific gravity 3·5–3·8. Composition: alumina 80·2 per cent, glucina or beryllia 19·8 per cent. Formula $BeO.Al_2O_3$.

Websterite, a hydrated aluminium sulphate, $Al_2(SO_4)_3.9H_2O$. An earthy white mineral. Hardness 1–2; specific gravity 1·66. Composition: alumina 29·8 per cent, sulphuric anhydride 23·2 per cent, water 47 per cent.

Wavellite. Cryst. system rhombic. Colour, white, cream and yellowish, also light brown. Lustre vitreous. Hardness 3·5–4; specific gravity 2·33. A hydrated aluminium phosphate, $3Al_2O_32P_2O_5.12H_2O$: alumina 37·3 per cent, phosphoric acid 34·4 per cent, water 28·3 per cent. *Turquoise* is a hydrated aluminium phosphate.

Qualitative Tests

Salt used: potash alum, $K_2SO_4Al_2(SO_4)_324H_2O$, or aluminium sulphate, $Al_2(SO_4)_3$.

1. Sulphuretted hydrogen in the presence of hydrochloric acid gives no precipitate.
2. Ammonium hydroxide causes a white gelatinous precipitate to form; insoluble in excess.

$$Al_2(SO_4)_3+6NH_4OH=2Al(OH)_2+3(NH_4)_2SO_4$$

3. Potassium and sodium hydroxides cause a white gelatinous precipitate to form; soluble in excess of the reagent to form the aluminate:

(i) $Al_2(SO_4)_3+6KOH=2Al(OH)_3+K_2SO_4$

and in excess of reagent:

(ii) $Al(OH)_3+3KOH=Al(OK)_3+3H_2O$

4. Ammonium sulphide gives a white gelatinous precipitate. The sulphide first formed is instantly decomposed to hydroxide, and the white precipitate which forms is aluminium hydroxide. The following equations express the three stages of this reaction:

(i) $Al_2(SO_4)_3+3(NH_4)_2S=Al_2S_3+3(NH_4)_2SO_4$

(ii) $Al_2S_3+6H_2O=3H_2S+2Al(OH)_3$

(iii) $Al_2(SO_4)_3+3(NH_4)_2S+6H_2O$
$$=2Al(OH)_3+3(NH_4)_2SO_4+3H_2O$$

With the borax bead, aluminium compounds give, in both the oxidizing and reducing blowpipe flames, colourless beads, and the same with microcosmic salt. When heated on charcoal in the oxidizing flame, and then moistened with cobalt nitrate, and again heated for some time, a beautiful bright-blue mass will result. This is unaffected by acids. Minerals such as alunogene, when heated in a closed tube, give off water and SO_3.

Quantitative Assays

The chief source of this metal is the mineral bauxite, which also contains iron and titanium. This mineral is very sparingly soluble in acids, and it is necessary to fuse it with $KHSO_4$ to effect solution. It is also very essential to grind the ore extremely finely before commencing the assay; otherwise it might be necessary to filter off the insoluble matter and repeat the fusion.

Weigh 1 gram of the sample into a platinum crucible and fuse with about 6 gram of potassium bisulphate. When cold place in a 400-ml. beaker, add about 20 ml. hot water, and then about 20 ml. strong HCl. Evaporate carefully to dryness on the hot plate, stirring occasionally to avoid spitting, and bake for half an hour. Cool, take up in dilute HCl, and filter through a No. 30 11-cm. Whatman paper. Ignite, filter, weigh, and return to platinum crucible. Add about 2 ml. HF, and two drops of 50-per-cent H_2SO_4, evaporate carefully to dryness, ignite, and weigh. Treat insoluble matter again with HF, and weigh as before. If the weight is constant, no further treatment is necessary (the loss in weight is silica), and any residue can be taken up with HCl and added to the filtrate from the insoluble matter.

To the filtrate add bromine water and ammonia in slight excess, and stand on the hot plate until the smell of ammonia is barely discernible. Filter through an open paper (No. 541 Whatman is suitable) and wash with hot water. Dissolve the precipitate, which consists of aluminium, iron and titanium hydroxides, together with traces of magnesia and lime, in HCl. Dilute and warm, and then add a large excess of caustic-soda solution, which will precipitate the iron and titanium, retaining the alumina in solution.

Filter off the combined precipitates, washing with hot water, and acidulate the filtrate with HCl. Now add a slight excess of ammonia, boil, and stand hot to settle. Filter through open paper, wash well with hot water, ignite, and weigh as Al_2O_3. Factor: 0·5291.

In ores of iron, manganese or zinc, which do not contain titanium, the following procedure might be adopted with advantage. Dissolve in a suitable quantity of HCl or aqua regia; evaporate to dryness and bake to render the silica insoluble. Take up with dilute HCl, filter, and wash with hot water. Add a few drops of HNO_3 to oxidize the iron, and then add dilute ammonia until a deep-red tinge is produced. Now add about 20 ml. strong ammonium-acetate solution, bring to the boil, and allow to settle.

Filter off the combined precipitates of iron and alumina, wash with hot water, and dissolve in HCl. Reprecipitate with slight excess of ammonia, and filter as before. The precipitate can now be redissolved and the alumina extracted with NaOH or, alternatively, it may be ignited and weighed. In the latter case, dissolve the ignited precipitate in HCl, estimate the iron by means of potassium bichromate, convert to Fe_2O_3, and subtract from the total weight of alumina and ferric oxide, the difference being Al_2O_3.

PHOSPHATE METHOD

This method is very suitable for ores not containing titanium, and has the advantage of avoiding the very tedious filtration of Al_2O_3.

The ore is dissolved and the silica removed in the usual way, any Group II metals being precipitated with H_2S. The filtrate is boiled to expel the excess gas and the iron oxidized with nitric acid. To the filtrate add ammonia and ammonium carbonate until a faint precipitate is formed, and clear with two or three drops of HCl. Now add 20-per-cent sodium-thiosulphate solution until the solution is colourless, 20 ml. 10-per-cent ammonium or sodium phosphate and about 5 or 6 gram sodium or ammonium acetate. Boil for half an hour and allow the precipitate to settle. Filter, wash with boiling water, dry, and ignite; weigh as $AlPO_4$. Factor: 0·2211.

CHROMIUM, Cr; atomic weight 52·0

WHEN pure, chromium is a hard, crystalline white metal, having a good lustre. The specific gravity is 6·92, melting point 1520° C. Chromium has three valencies, 2, 3 and 6, and enters into an important class of products known as ferrochromium alloys. Chromous oxide, CrO, and its salts are easily converted by oxidation processes into chromic oxide, Cr_2O_3, and its salts. Chromium also forms an acid anhydride, chromium trioxide, CrO_3. There is only one mineral of importance known as *Chromite* or *Chrome-ironstone*. Cryst. system cubic, usually found massive. Fracture uneven. Hardness 5·5; specific gravity 4·3–4·5. A complex mineral of iron, chromium and magnesium, with small proportions of alumina $(FeOMgO)(Cr_2O_3)$: chromic oxide 40–64 per cent, ferrous oxide 18·5–38 per cent, alumina 2·19 per cent, magnesia 5·5–18 per cent.

Picotite. An iron, chromium, aluminium, magnesium compound $(MgFe)(AlFeCr)_2O_3$. In both *Chrome Ironstone* and *Picotite*, silica also occurs in small amounts from 0·5–2·2 per cent.

Crocoisite, $PbCrO_4$, has already been mentioned under lead.

Chrome-ochre is chromium sesquioxide, Cr_2O_3.

Redingtonite is a hydrated sulphate.

Qualitative Tests

Salt used: chromic sulphate, $Cr_2(SO_4)_3$.

1. Sulphuretted hydrogen gives no precipitate.
2. Ammonium sulphide causes a greyish-green precipitate of chromic hydroxide to form; soluble in cold hydrchloric acid:

$$Cr_2(SO_4)_3+3(NH_4)_2S+6H_2O=2Cr(OH)_3+3(NH_4)_2SO_4+3H_2O$$

This hydroxide is formed in the same way as previously described under aluminium.

3. Potassium and sodium hydroxides, also ammonia, give a greyish-green precipitate. The presence of citric and tartaric acids interferes with this reaction:

$$Cr_2(SO_4)_3+6NH_4OH=2Cr(OH)_3+3(NH_4)_2SO_4$$

4. To a solution of the above salt, add bleaching powder and boil. This causes the formation of a chromate salt. To this add lead acetate solution: a yellow precipitate of lead chromate will form:

(i) $Cr_2(SO_4)_3+6CaOCl_2+3H_2O=2H_2CrO_4+6CaCl_2+3H_2SO_4$

(ii) $H_2CrO_4+(CH_3COO)_2Pb=PbCrO_4+2CH_3COOH$

5. Sodium hydrogen phosphate in the presence of sodium acetate or ammonium acetate causes a pale-green precipitate of chromic phosphate, $Cr_2(PO_4)_2$, to form; soluble when freshly prepared in hot acetic acid, and also in hydrochloric acid. If citric or tartaric acids are present precipitation is prevented.

6. With the borax bead a yellowish-green bead is produced in the oxidizing flame, grass-green when cold; and in the reducing flame the bead is green when hot and emerald-green when cold.

With microcosmic salt the bead in the oxidizing flame is reddish-green when hot and emerald-green when cold; and in the reducing flame reddish-green when hot and green when cold.

Quantitative Assay

The estimation of chromium is based on the oxidation of a ferrous salt to the ferric state and the estimation of the excess ferrous iron added.

To effect solution, the mineral, which must be very finely divided, is fused with sodium peroxide, and, since nickel and a large quantity of iron are both very difficult to deal with—the former because the end-point in the subsequent iron determination is spoilt by the green tinge of the solution—it is preferable to carry out the fusion in a second-grade porcelain crucible, which can, however, only be used for one determination. Procedure is as follows: Weigh into the crucible 0·5 gram of the mineral and mix intimately with about 7 gram of sodium peroxide. Allow the crucible to stand on a pipeclay triangle over a moderate bunsen flame until fused; then, holding with a pair of tongs, gently rotate over the burner for about 2 minutes. Stand the crucible aside to cool, tilted, and then place in a 600-ml. beaker containing about 250 ml. hot water. When the action has subsided, boil on the hot plate for half an hour, cool somewhat, and add a slight excess of 20-per-cent H_2SO_4. Rinse out the crucible, add 50 ml. standard $FeSO_4$ solution, and titrate the excess ferrous iron with standard potassium bichromate.

TITANIUM, Ti; atomic weight 47·90

TITANIUM up to about twenty-five years ago was looked upon as a rare element in spite of the fact that it was very widely distributed in small amounts in conjunction with iron ores and clays, being found in an amorphous grey condition. The metal is silver-white, but it is doubtful whether it is absolutely pure. In the amorphous state the specific gravity is 4·5. The melting point is very high, 1800–1850° C., and for this reason titaniferous iron ores were found useless in connection with iron smelting. When heated in the air titanium burns with a bright flame, forming the dioxide.

One of the chief sources of titanium oxide today is the mineral *Rutile*, TiO_2. Cryst. system tetragonal, and frequently found in conjunction with quartz. Colour, red, reddish-brown, yellow and sometimes black. Fracture uneven or subconchoidal. Lustre usually metallic, sometimes a diamond-like or adamantine lustre. Hardness 6–6·5; specific gravity 4·18–4·24. Composition: titanium oxide 96–98 per cent, with small amounts 1–2·5 per cent. of iron oxide.

Ilmenite, $FeTiO_3$. A titaniferous iron ore. Cryst. system rhombohedral. Colour, iron-black, slightly magnetic. Fracture conchoidal. Hardness 5–6; specific gravity 4·5–5·0. Composition: ferrous oxide, FeO, 47·4 per cent, titanic oxide, TiO_2, 52·6 per cent.

Anastase, TiO_2, differs from rutile, which has just been mentioned, as regards its crystalline formation, being chiefly in tetragonal pyramids; Colour, brown, blue-back and black.

Sphene also known as *Titanite*. Cryst. system monoclinic, usually found as oblique rhombic prisms. Occurs in various colours, yellow, yellowish-green, brown, brownish-grey, grey and black. Lustre resinous or adamantine. Fracture conchoidal. Hardness 5–5·5; specific gravity 3·4–3·56. Composition, titanium and calcium silicate, $CaO.2SiO_2 + CaO.2TiO_2$: titanium oxide 33–43 per cent, lime 21–33 per cent, silica 30–35 per cent. Small amounts of manganese may also be found present.

Menaccanite, $Fe_3O_4.TiO_2$, is another titaniferous iron ore.

Qualitative Tests

Salt used: titanium dioxide, TiO_2.

1. On fusing with potassium hydrogen sulphate the dioxide is converted into sulphate, which is soluble in water and can be used for further confirmation tests. The powdered ore can also be fused with potassium pyrosulphate until it ceases to effervesce, and, when cold, dissolved in boiling 10-per-cent H_2SO_4.
2. Potassium and sodium hydroxides cause a voluminous white precipitate, $Ti(OH)_4+xH_2O$, to form. Soluble in ammonium carbonate, but reprecipitated on boiling for some time.
3. Hydrogen peroxide produces a yellow coloration when sulphuric or hydrochloric acids are present in the solution. On adding zinc dust the liquid is decolorized.
4. Dihydroxymaleic acid gives a reddish-brown coloration, and if the solution is a concentrated one a chocolate-brown precipitate of titanium dihydroxymaleic acid; insoluble in acids, except hydroflouric acid.

Quantitative Assay

The commonest ore of titanium is the mineral ilmenite, or titaniferous iron ore. This material is almost insoluble in HCl, so that it is necessary to fuse the finely ground sample with potassium bisulphate to effect solution.

From 0·5 to 1 gram of the mineral is weighed into a platinum crucible containing about 6 gram of $KHSO_4$, and the contents well mixed by stirring with a thin glass rod. The crucible is held over a low bunsen flame in a pair of iron tongs, and when the water has been removed the temperature is raised and the contents of the crucible gently rotated. When fusion is complete, as shown by the absence of dark particles in the melt, the crucible is removed from the flame and allowed to cool on its side. The melt, which can usually be removed whole by gently squeezing the side of the crucible, is transferred to a 250-ml. beaker, the crucible being rinsed with boiling water and the rinsings added to the beaker. A little more water is added if necessary to effect solution, and the insoluble matter is filtered off. It is sometimes necessary to treat the insoluble residue with more bisulphate.

To the filtrate ammonia is added until nearly neutral, and the solution is diluted to about 450–500 ml. A strong solution of sodium sulphite is now added in excess, which will reduce the iron to the ferrous state. The solution is boiled until free from SO_2, preferably for at least 2 hours, during which time the titanium is precipitated as the hydrated dioxide, $TiO_2.H_2O$. The precipitate is allowed to settle, filtered through a close paper, well washed with hot water, and ignited. The residue is TiO_2, which contains 60·051 per cent Ti.

MOLYBDENUM, Mo; atomic weight 96·0

THIS element is divalent, trivalent, tetravalent, pentavalent and hexavalent. It is not found in very large quantities, and is quite a rare mineral. Molybdenum is a hard white metal with a very high melting point, 2250° C., and specific gravity 9·1. It is quite soluble in nitric acid, aqua regia and concentrated sulphuric acid. Molybdenous oxide, MoO, is black, so also is sesquioxide, Mo_2O_3, while the dioxide, MoO_2, is usually brown, sometimes dark violet. All of these oxides, when treated with nitric acid, are converted into the trioxide MoO_3. The chief ores of molybdenum are *Molybdenite*, a sulphide, MoS_2, *Molybdine* or *Molybdic Ochre*, MoO_3, and *Wulfenite*, lead molybdate, $PbMoO_4$.

Molybdenite. Cryst. system hexagonal. Commonly found massive, sometimes found granular, at other times foliated. Hardness 1–1·5, easily scratched by the finger nail; specific gravity 4·4–4·8. Molybdenum 57–59 per cent, sulphur 39–40 per cent. Found at Brandy Gill, Cumberland, and in some of the Cornish mines; at Auerbach in Saxony, in the Urals, and in the states of New Hampshire and Pennsylvania, U.S.A.

Molybdic Ochre or *Molybdine.* Cryst. system rhombic, when as molybdic acid, MoO_3, the oxide is produced in the laboratory. In nature it is found as incrustations or as a powder, or occasionally in a silky-fibrous mass. Colour, light yellow, sometimes yellowish-white. Hardness 1–2; specific gravity 4·4–4·5. Composition: molybdenum 65·71 per cent, oxygen 34·29 per cent. Found at Coldbeck Fell and Carrock, Cumberland, also associated with molybdenite in situations previously mentioned.

Qualitative Tests

Salt used: molybdic acid, H_2MoO_4.

1. Sulphuretted hydrogen in the presence of HCl gives a brownish-black precipitate of molybdenum sulphide, MoS_3, which is soluble in alkaline sulphides.
2. A solution of molybdic acid treated with excess of NH_4OH, and then with yellow ammonium sulphide forms a brownish-black

precipitate of molybdenum sulphide after boiling the liquid for some time.

3. Potassium ferrocyanide added to a molybdate solution in the presence of HCl causes a reddish-brown precipitate of molybdenum ferrocyanide to form.
4. If an alcoholic solution of diphenyl carbazide is added to a weak alkaline molybdate solution, an indigo-violet coloration is produced: an excess of alkali destroys the colour.

When molybdenite is powdered finely and then heated on charcoal in the oxidizing flame, it gives off a strong smell of SO_3, and an incrustation of molybdic acid is produced. When treated in an open tube, sulphurous fumes are given off. Molybdenum compounds colour the bunsen flame yellowish-green. Molybdenite might be mistaken for graphite, but can easily be distinguished from graphite by its solubility in nitric acid, and the evolution of SO_3 fumes when heated. Graphite is insoluble in nitric acid.

Quantitative Assay

A suitable quantity of the finely ground mineral is dissolved in HNO_3, evaporated to dryness, and baked. When cool, 5 ml. HNO_3 is added, and then about 20 ml. hot water, the beaker warmed until solution is complete, and the iron precipitated with ammonia. After removal of the iron, which should be dissolved and reprecipitated if necessary, the solution is acidulated with acetic acid, a sufficient excess being added to replace all the HNO_3, a little ammonium acetate also being added. The solution is now brought to the boil and titrated hot with standard lead-acetate solution.

For an indicator, a freshly prepared solution of tannic acid is used, drops being set out on a white porcelain plate. A little of the solution under test is withdrawn from time to time by placing the forefinger over the end of the stirring tube and allowed to mix with the drops of tannic acid on the plate. The end-point is reached when no further coloration is observed, a brilliant yellow colour being produced until the molybdenum is exhausted. Should no precipitate be observed at the commencement of the titration, 20 ml. of the lead solution is run in and the solution allowed to stand hot for an hour, after which it is filtered through a No. 42 or 32 Whatman paper, washed well with hot water until free from lead (a little sodium-sulphide solution in a test tube should be placed under the funnel; any lead remaining in the washings will be precipitated as black lead sulphide), ignited in a porcelain crucible, and weighed as $PbMoO_4$.

TUNGSTEN, W; atomic weight 183·92

TUNGSTEN, otherwise known as *Wolframium*, is obtained by reducing the trioxide, WO_3, with hydrogen, aluminium or carbon at a high temperature, when an iron-grey powder, specific gravity 19·1 and melting point 3400° C., is obtained. The two chief minerals containing this element are *Wolfram* and *Scheelite*.

Wolfram. This mineral is frequently found associated with tin ores. Cryst. system monoclinic. Colour, greyish-black. Fracture uneven. Hardness 5–5·5; specific gravity 7·1–7·8. A complex mineral consisting of iron and manganese tungstates, $2FeWO_4.3MnWO_4$: ferrous oxide 9–20 per cent, manganous oxide 4–14 per cent and tungstic acid 75–76 per cent. In this mineral the amounts of iron and manganese found in different deposits depends on the ratio of the iron tungstate to the manganese tungstate. Found at Brandy Gill, Cumberland, and in several of the old tinstone mines in Cornwall; also in the states of Connecticut, Missouri and Carolina, U.S.A.

Scheelite. Cryst. system tetragonal. A brittle mineral of uneven fracture, which is usually subconchoidal. Colour, usually yellowish-white or light brown. Hardness 4·5–5·0; specific gravity 5·9–6·07. Composition: lime 18–19 per cent, tungstic acid 76–80 per cent. Found at Brandy Gill, Cumberland; frequently associated with wolfram and molybdenite; also in many Cornish tinstone mines, in the Harz mountains, Siberia, and the state of Connecticut, U.S.A.

Tungstite or *Tungstic Ochre*, WO_3. Found in an earthy state due to a process of degradation. Colour, yellow or yellowish-green. Composition: tungsten 79·3 per cent, oxygen 20·7 per cent. Practically pure tungstic acid. Found at Carrock Fell, Cumberland.

Other minerals containing tungsten are *Stolzite*, $PbWO_4$, and *Cuprotungstite*, $CuWO_4$, but both are rare and do not occur in the British Isles.

Qualitative Tests

Salt used: Sodium tungstate, $Na_2WO_4.2H_2O$.

1. Sulphuretted hydrogen produces hardly any precipitate in the presence of an acid solution.
2. Potassium ferrocyanide gives a deep brownish-red coloration after a few drops of HCl have been added, and, on allowing the tube to stand, a precipitate will form after some time.
3. On the addition of stannous chloride to a solution of an alkaline tungstate a yellow precipitate will form. If hydrochloric acid is

now added, and the tube is heated, the precipitate will turn bright blue.

4. On the addition of ferrous sulphate, a yellow precipitate will form, but on the addition of hydrochloric acid no blue precipitate or coloration will be produced.
5. Scheelite, when fused with microcosmic salt in the reducing flame, forms a green bead which becomes blue on cooling. Should iron be present, the mineral should be fused on charcoal with a little metallic tin, otherwise no blue colour will be produced. Tungstite or tungstic ochre is soluble in alkaline solutions of KOH or NaOH, but is insoluble in acids.

Quantitative Assay

Quite the best method for the estimation of this metal is the modification of Hutchin and Tonk's method proposed by Wraight. A suitable quantity of the material is fused with five or six times its weight of potassium bisulphate in a platinum dish. When fusion is complete, the dish is allowed to cool, and the melt extracted with about 100 ml. boiling water containing a little H_2SO_4. The tungsten, which will have been precipitated as tungstic oxide, is filtered on to a close paper, washed with hot water, and then redissolved by washings of ammonia, the filtrate being collected in a clean beaker. The filtrate is diluted to about 200 ml. and made slightly acid with HNO_3. The tungsten is now precipitated with about 20 ml. of saturated mercurous-nitrate solution, the solution warmed somewhat, and a few drops of ammonia added. After stirring, the precipitate is allowed to settle, filtered, washed with dilute mercurous-nitrate solution, ignited, and weighed as WO_3. Factor: 0·7931.

ZINC, Zn; atomic weight 65·37

ZINC is divalent. It is a bluish-white, very lustrous metal, which soon tarnishes in the air due to the surface becoming coated with basic zinc carbonate. In the cold it is hard and brittle, but between 100° C.–150° C. it becomes ductile. The specific gravity is 6·9–7·2, and it melts at 418° C. and boils at 929° C., burning with a bluish-green flame, and giving off fumes of zinc oxide on coming in contact with the air. Zinc oxide is an important pigment, creamy-white in colour; insoluble in water, but readily soluble in hydrochloric, nitric, sulphuric and glacial acetic acids.

Blende or *Black Jack*, ZnS, is one of the most important ores of zinc. Cryst. system cubic, usually found as octahedra and rhombic-dodecahedra, and often twinned. Is found massive, fibrous and as spheroidal aggregations. Colour, black or brownish-black. Fracture conchoidal. A brittle mineral. Hardness 3·5–4; specific gravity 3·9–4·2. Composition: zinc 67·00 per cent, sulphur 33·00 per cent. A zinc sulphide, ZnS. A variety of blende known as *Wartsite*, ZnS, has a resinous lustre with a brownish-black colour. In mineral veins blende is frequently associated with galena, barytes, chalcopyrite, and $Cu_2S.Fe_2S_3$. Blende is found at Thornthwaite in Cumberland, also at Woodend in the same county; in Cornwall and Derbyshire; the Harz mountains, Saxony, Belgium, Sweden, Australia; and in the United States in the states of Missouri and Wisconsin; and in many other parts of the world.

Calamine or *Smithsonite*, $ZnCO_3$, known to the miners as dry bone. Cryst. system rhombohedral. Found in various forms as massive, kidney-shaped, stalactitic, granular, in spherical aggregations or botryoidal and earthy. A very important ore of zinc. Found in various colours: white, grey, greyish-white, brown and greenish-brown. Lustre vitreous. Fracture uneven. Hardness 5; specific gravity 4–4·45. Composition: zinc oxide 64·8 per cent and carbon dioxide 35·2 per cent. Found at Raughtengill and Alston Moor, Cumberland; near Matlock in Derbyshire; the Mendip Hills, Somerset; in Cornwall; Donegal, Northern Ireland; Silesia, Spain, Nortschinsk, in Siberia; in Pennsylvania and Missouri, U.S.A.; and Australia.

Zincite or *Red Zinc Oxide*, ZnO. Cryst. system hexagonal. Cleavage basal and perfect. Found chiefly massive and granular, sometimes foliated. A beautiful mineral, varying in colour from light yellow to bright red, frequently translucent and semi-opaque. Lustre brilliant to adamantine. Fracture subconchoidal. Hardness 4–4·5; specific gravity 5·4–5·75. Composition: zinc 80·30 per cent, oxygen 19·70 per cent. Found in the Franklin mines, New Jersey, U.S.A.

Hydrozincite or *Zinc Bloom*. A hydrated variety of zinc carbonate, appearance dull. Colour, whitish-grey to yellow. Specific gravity 3·69–3·80, $ZnCO_3.2Zn(OH)_2$. Composition: zinc oxide 75·30 per cent, carbon dioxide 13·60 per cent, water 11·10 per cent. Found at Alston Moor, Cumberland.

Hemimorphite or *Electric Calamine*. Silicate of zinc. Cryst. system rhombic. Frequently found as modified rhombic prisms; often found twinned. Colour, white, yellowish-brown and bluish-green. Lustre vitreous. Fracture uneven, when heated becomes electric. Hardness 4·5–5; specific gravity 3·16–4. Composition ($2ZnO.SiO_2.H_2O$): zinc oxide 67·5 per cent, silica 25 per cent, water 7·5 per cent. Found in various parts of the British Isles; Mendip Hills, Somerset; Matlock and Castleton, Derbyshire; Alston Moor and Raughtengill, Cumberland; near Holywell, North Wales; Leadhills in Scotland; in Belgium, Silesia, Hungary, and many parts of the United States.

Auricalcite. This is a hydrated carbonate of zinc and copper. Colour, pale-green to sky-blue. Lustre pearly. Specific gravity 3·6. Formula: $2(ZnCu)CO_3.3(ZnCu)(OH)_2$. Composition: zinc oxide 53·2 per cent, copper oxide 20·8 per cent, carbon dioxide 16·1 per cent, water 9·9 per cent. A rare mineral. Found as museum specimens at Raughtengill, Cumberland.

Goslarite or *Zinc Vitriol.* Cryst. system rhombic; usual form rhombic prisms, sometimes found incrusting and stalactitic. A brittle vitreous mineral, white in colour. Hardness 2–2·5. Composition ($ZnSO_4.5H_2O$, a hydrated zinc sulphate): zinc oxide 28·2 per cent, sulphates 27·9 per cent, water 43·9 per cent. A zinc mineral produced by the decomposition of zinc blende. Occurs in Sweden and Austria. Specimens have been found at Holywell, North Wales.

Willemite. Found in the mines of New Jersey, U.S.A. A silicate of zinc, Zn_2SiO_4. Hardness 5–5·5; specific gravity 4–4·1. Colour, usually yellowish-brown.

Troostite. A rare zinc silicate where some of the zinc is replaced by manganese. A typical detailed analysis is as follows:

Zinc oxide, ZnO	57·50	per cent
Manganese oxide, MnO	12·60	"
Silica, SiO_2	27·90	"
Ferrous oxide, FeO	0·62	"
Magnesia, MgO	1·12	"
Moisture	0·26	"
	100·00	

Franklinite. This is a most important mineral in the mines of New Jersey, U.S.A., worked for zinc by the New Jersey Zinc Co., Inc., and from which most of the zinc oxide is produced. It has a sub-metallic lustre. Colour, iron-black. Cryst. system cubic, usually found octahedral; may also be found massive and granular. Fracture conchoidal. Hardness 5·5–6·5; specific gravity 4·85–5·112. A complex ore of iron, zinc and manganese oxides:

A typical detailed analysis is:

Zinc oxide, ZnO	19·40	per cent
Ferric oxide, Fe_2O_3	60·50	"
Ferrous oxide, FeO	0·50	"
Manganic oxide, Mn_2O_3	6·80	"
Manganous oxide, MnO	12·80	"
	100·00	"

Qualitative Tests

Salt used: zinc sulphate, $ZnSO_4.7H_2O$.

1. Sulphuretted hydrogen in the presence of hydrochloric acid gives no precipitate.
2. Ammonium sulphide causes a white precipitate of zinc sulphide to form; insoluble in acetic acid, but readily soluble in dilute hydrochloric acid:

   $$ZnSO_4+(NH_4)_2S=ZnS+(NH_4)_2SO_4$$

3. Potassium and sodium hydroxides, also ammonia, cause a gelatinous white precipitate to form, which is soluble in excess forming zincates:

   (i) $ZnSO_4+2KOH=Zn(OH)_2+K_2SO_4$
   (ii) $Zn(OH)_2+2KOH=Zn(OK)_2+2H_2O$

4. Potassium ferrocyanide causes a white precipitate of zinc ferrocyanide to form; insoluble in dilute acids:

   $$2ZnSO_4+K_4Fe(CN)_6=Zn_2(Fe(CN)_6)+2K_2SO_4$$

5. Potassium ferricyanide causes an orange precipitate to form, soluble in hydrochloric acid:

   $$3ZnSO_4+2K_3Fe(CN)_6=Zn_3(Fe(CN)_6)_2+3K_2SO_4$$

6. A zinc salt or zinc mineral when mixed with sodium carbonate and heated on charcoal in the reducing flame, forms a deposit of zinc oxide, which is yellow when hot but white on cooling.

When a powdered mineral, such as blende, is heated on charcoal with a reducing flame, and is then moistened with cobalt nitrate solution, a green incrustation of cobaltizincate, $CoZnO_2$, is produced.

Quantitative Assay

Weigh 1 gram of the finely ground mineral into a 250-ml. squat beaker and dissolve in about 25 ml. strong HCl (if much lead is present a little potassium chlorate will assist). Cool, and add about ½ ml. of bromine. Make up to about 50 ml. with boiling water. Precipitate iron and manganese with dilute ammonia (50 : 50) and boil for a few minutes. Allow to settle, and filter through a No. 4 or 31 11-cm. Whatman paper, collecting filtrate in a 600-ml. conical flask, and wash with hot water and ammonia. Wash back the precipitate into the original flask (do not acidify paper) and dissolve in HCl. Precipitate iron as before and filter through the same paper, combining the two filtrates. Acidify filtrate with HCl (if no copper is present use litmus paper) and add 3 ml. in excess. Add about 1 gram of fine test lead and boil gently for half an hour to precipitate any copper present—if desired 20 ml. of saturated H_2S water added immediately before the titration will serve the same purpose. Titrate boiling with standard potassium-ferrocyanide solution, using drops of 10-per-cent uranium acetate or nitrate as an indicator on a porcelain plate. An excess of the standard solution is shown by the brown coloration imparted to the indicator. It will be found very convenient if a glass tube is used for a stirring rod, the end being protected by about an inch of rubber tubing. Sufficient solution can be withdrawn by placing the forefinger over the end of the tube when testing for the end-point. This procedure is suitable for all titrations where an outside indicator is used.

The titration can also be carried out using diphenylamine or diphenylbenzidene as internal indicator.

MANGANESE, Mn; atomic weight 54·93

THIS element occurs in five different valencies, viz.: divalent, trivalent, tetravalent, hexavalent and heptavalent. The colour of manganese is greyish-white. It is a hard and brittle metal; soluble in acids. Specific gravity 7·2, melting point 1230° C., boiling point 1900° C. Manganous oxide or monoxide, MnO, is light green in colour. Manganic oxide, Mn_2O_3, is brownish-black in colour. The dioxide, MnO_2, is black and dissolves in hydrochloric acid, chlorine being evolved.

Pyrolusite, MnO_2. Cryst. system rhombic. Often occurring as small rectangular prisms, structure frequently massive or kidney-shaped (reniform). Colour, black or steel-grey. Lustre metallic. Hardness 5·2–5·4; specific gravity 4·8–5. Composition: manganese 63 per cent, oxygen 37 per cent, MnO_2. Found in England in mines near Callington, Cornwall, and in Devon; also Westphalia, Spain and the United States, in Massachusetts and Connecticut.

Psilomelane. Found in various forms, sometimes massive, kidney-shaped, amorphous, spheroidal aggregations. Colour, black or dark-grey. Lustre submetallic. Hardness 5–6; specific gravity 3·7–4·7. Nearly always associated with barytes, heavy spar or barium sulphate. A hydrated manganese peroxide, $x\mathrm{MnO}.y\mathrm{BaO}.x\mathrm{MnO_2}.\mathrm{H_2O}$. Composition: manganese oxides 69–80 per cent, oxygen 5–15 per cent, barium oxide 0–17 per cent, water 0–6 per cent. Found in Cornwall; Force Crag mine, near Keswick, Cumberland; near Tavistock, Devon; Harthill, Warwickshire; Leadhills, Scotland; and in the state of Vermont, U.S.A.

Hausmannite. Cryst. system tetragonal; usual form octahedral, and often found twinned. Colour, brownish-black. Fracture uneven. Hardness 5–5·5; specific gravity 4·70. Composition: manganous oxide 31·0 per cent, sesquioxide 69·0 per cent, $MnO.Mn_2O_3$.

Wad. Usually amorphous or earthy. Colour, black or brownish-black. Hardness 0·4–0·6; specific gravity 3–4·26. A decomposition product. Found at Millbeck Gill, Cumberland, and other places where manganese ores occur.

Manganite. Cryst. system rhombic, usually as rhombic prisms. Colour, black or dark grey. Fracture uneven. Hardness 4; specific gravity 4·2–4·4. Composition: manganese 62·5 per cent, oxygen 27·5 per cent, water 10 per cent. A hydrated manganese sesquioxide, $Mn_2O_3.H_2O$. Found at Force Crag mine, Cumberland; in several mines in Cornwall; Mendip Hills, Somerset; in Sweden, Norway and in several parts of Canada around New Brunswick.

Rhodonite or *Manganese Spar.* Cryst. system triclinic. Nearly always occurs massive. Colour, light red with a brownish tinge; also yellow and greenish. Lustre vitreous. Fracture uneven, sometimes conchoidal. Hardness 5·5–6·5; specific gravity 3·4–3·6. A manganese silicate, $MnO.SiO_2$: manganous oxide 54 per cent, silica 46·0 per cent. Found near Callington, Cornwall, in conjunction with Swedish iron ore, Fe_3O_4; also in the Harz mountains in Siberia, and in Massachusetts, U.S.A.

Qualitative Tests

Salt used: manganese sulphate, $MnSO_4.4H_2O$.

1. Sulphuretted hydrogen in the presence of hydrochloric acid gives no precipitate.
2. Ammonium sulphide causes a salmon-pink precipitate of manganous sulphide to form, soluble in cold dilute hydrochloric acid (distinction from nickel and cobalt). It is also soluble in acetic acid (distinction from zinc sulphide). Warming the solution accelerates precipitation:

$$MnSO_4+(NH_4)_2S=MnS+(NH_4)_2SO_4$$

3. Potassium and sodium hydroxides, also ammonia, cause a white precipitate to form. In the case of potassium and sodium hydroxides, the precipitates are insoluble in excess, and on boiling the manganous hydroxide is converted into dark-brown manganic hydroxide, $Mn(OH)_3$. In the case of ammonia the hydroxide is soluble in excess of ammonium chloride:

(i) $MnSO_4+2NH_4OH=Mn(OH)_2+(NH_4)_2SO_4$

(ii) $2Mn(OH)_2+H_2O+O=2Mn(OH)_3$

4. A solution of bleaching powder, $CaOCl_2$, causes a brown precipitate of hydrated manganese dioxide to form:

   $MnSO_4+CaOCl_2+Ca(OH)_2=MnO_2+CaCl_2+CaSO_4+H_2O$

5. Manganese salts heated with borax give a red-violet bead with the oxidizing flame, a similar bead with microcosmic salt and a colourless bead with the reducing flame.

Compounds of manganese when mixed with sodium carbonate, heated at first gently to expel moisture and then more strongly, yield a green mass of manganate. A better and more rapid result is obtained if potassium nitrate is used in addition to the carbonate.

Quantitative Assay

BASIC ACETATE METHOD (Volhard's Method)

This method is regarded as the standard assay for manganese and, while it might be considered as rather tedious, it has the advantage of absolute accuracy no matter what particular grade of ore is under examination. Where Volhard's method is used for routine assays (in which case an ore of known value is used to check the standard solution), the percentage of Mn in the check sample should always be determined either by this method or by difference in the complete analysis—preferably both ways.

Weigh out from 0·3 to 0·5 gram of the finely ground mineral and dissolve in a little HCl. Add 10 ml. of dilute (50-per-cent) H_2SO_4 and evaporate to fuming point. Take up the residue in a little water, dilute to about 50 ml. and then add a slight excess of pure zinc oxide to precipitate the iron. Boil for a few minutes, allow to settle, and filter, washing well with hot water.

Now add about 5 gram of ammonium acetate, and about 2 ml. of bromine—not bromine water. Boil for a few minutes, and allow to settle. The manganese will be precipitated as oxyhydrate, $MnO(OH)_2$. Filter, wash well with hot water, until the drainings from the funnel are free from bromine, then place filter paper and precipitate back into the original beaker. Add a measured excess of decinormal oxalic acid, and about 20 ml. of dilute H_2SO_4. Dilute to about 250 ml. with hot water, and titrate the excess oxalic acid with decinormal potassium permanganate. Before completing the assay, the filtrate from the oxyhydrate precipitation should always be tested to ensure the total recovery of the manganese. This can be done by adding another 2 ml. of bromine, and boiling again for a further minute or two.

Where rich ores are to be tested it is sometimes advisable to weigh out 5 gram of ore, dissolve in HCl, make up to 250 ml. in a measuring flask, and pipette out duplicate trials of, say, 15 ml. each.

MANGANESE ORES

The following modification of Volhard's method is very useful where routine estimations of similar grades of ore are to be tested, as would be the case on a manganese-ore mine. For standardization purposes a sample should be taken, whose Mn content has been determined by the basic acetate method and by difference from the complete analysis of the ore. The procedure is as follows:

Weigh 0·5 gram of the sample (powdered) into a 600-ml. tall beaker; add 25–30 ml. HCl, and stew gently on the hot plate. When dissolved, add 8 or 9 drops of HNO_3, boil for 10 minutes, and rinse beaker and cover well with hot water. Boil and repeat, rinsing twice. Then remove cover and add pure zinc oxide (use a horn spatula) little by little until the iron is precipitated, adding a little excess, which should be about the size of a shilling, on the bottom of the beaker. Make up to about 350 to 400 ml. with boiling water and titrate with potassium permanganate (a 1-per-cent solution is approximately equivalent to 5 mg. Mn per ml.).

Considerable care must be used when stirring the solution to avoid breaking up the precipitate too much, and the " bobby " can be used to clean the side of the beaker near the top of the solution. At the end-point the solution should be stirred vigorously and, when quiet, a few more drops of permanganate should be added if the pink colour has faded.

COLORIMETRIC ESTIMATION OF MANGANESE IN STEEL AND IRON

For this assay a series of standard samples are required, ranging from low to high manganese contents.

The procedure is as follows: 0·2 gram of the sample is dissolved in 20 ml. of HNO_3 (s.g., 1·2) in the cold; 10 ml. of silver-nitrate solution (1·38 gram per litre) is added and the solution made up to 100 ml. and well mixed. Of this solution 10 ml. is placed in a glass, stoppered, and 2·5 ml. of 20-per-cent ammonium-persulphate solution is added.

The test tube is placed in water at between 80–90° C. and allowed to remain in the water until the bubbles of gas become more numerous and remain at the top for a few seconds. The tube is then cooled and the colour compared with that of standard samples treated in exactly the same way.

NICKEL, Ni; atomic weight 58·68

THIS element is divalent, also trivalent and tetravalent. Metallic nickel is greyish-white in colour, hard and lustrous. The specific gravity is 8·8, and the melting point 1452° C. Nickel enters into several alloys, such as German silver, which is a brass containing nickel, from 6–30 per cent; also nickel-steel, which contains 3–5 per cent of nickel, as well as several combinations of copper and nickel, like monel metal, which consists of copper 30 per cent and nickel 70 per cent; also in coinage.

Kupfernickel or *Arsenical Nickel*. Cryst. system hexagonal, usually found massive. Colour, pale copper-red, hence the name kupfernickel or copper nickel. Fracture uneven. Hardness 5·5; specific gravity 7·3–7·4. Composition: nickel 44·1 per cent, arsenic 55·9 per cent; often associated with antimony, iron, cobalt. Also known as *Nickelite*, NiAS.

Breithauptite. Cryst. system hexagonal. Colour, copper-red, has a metallic lustre and is an antimonial-nickel ore associated with lead sulphide. Hardness 5·5; specific gravity 7·5. Composition: nickel 21·25 per cent, antimony 78·75 per cent, NiSb.

Chloanthite, also known as *White Nickel*, $NiAS_2$. Cryst. system cubic. Colour, white. Hardness 5·5–6; specific gravity 6·4–6·6. Composition: nickel 28·40 per cent, arsenic 70·35 per cent. Nickel arsenide. When some of the nickel is replaced by cobalt, becomes greyish-white.

Millorite or *Millerite*, also known as *Nickel Pyrites*, NiS. Cryst. system rhombohedral. Colour, bronze-yellow. Lustre metallic. Hardness 3–3·5; specific gravity 4·6–5·5. Composition: nickel 64·9 per cent, sulphur 35·1 per cent. Often associated with small quantities of copper, cobalt and iron.

Other minerals containing nickel are *Zaratite*, hydrated nickel carbonate, $NiCO_3.6H_2O$, often found associated with chrome ironstone; *Ullmanite*, a nickel-antimony sulphide, NiSbS, and *Gersdorffite*, a nickel-arsenic sulphide, NiAsS.

Qualitative Tests

Salt used: nickel sulphate, $NiSO_4.6H_2O$.

1. Sulphuretted hydrogen in the presence of hydrochloric acid gives no precipitate.
2. Ammonium sulphide causes a black precipitate of nickel sulphide to form. The sulphide is slightly soluble in excess, but entirely

precipitated on boiling. The top liquid has a brown cast, due to this slight solubility:

$$NiSO_4+(NH_4)_2S=NiS+(NH_4)_2SO_4$$

3. Sodium and potassium hydroxides and ammonia cause a precipitate of nickel hydroxide to form. Potassium and sodium hydroxides give a gelatinous apple-green precipitate unaltered by boiling (distinction from cobalt) and insoluble in excess of the reagent. Ammonia also gives a greenish precipitate which, due to the formation of a basic compound when the ammonia is added in excess, changes to a bluish solution:

$$NiSO_4+2NaOH=Ni(OH)_2+Na_2SO_4$$

4. Potassium cyanide produces a greenish-yellow precipitate of nickelous cyanide; soluble in excess. If a drop or two of hydrochloric acid is added, the liquid boiled in a fume cupboard (if necessary more HCl is added until all fumes of hydrocyanic acid have been eliminated), and then sodium hydroxide is added, a precipitate of nickel hydrate is produced.
5. Potassium nitrite when added to a neutral solution of a nickel salt, and an excess of acetic acid added, produces no precipitate on the addition of potassium acetate and 80 per cent alcohol even on standing. This is a very useful method for separating nickel from cobalt when associated together. (See Cobalt.)

Heating on charcoal, in the reducing flame, yields a black magnetic powder of nickel. The borax bead heated in the oxidizing flame is violet when hot and brown when cold. With the reducing flame a greyish bead is obtained after heating for some time. With microcosmic salt a yellow bead is produced in the oxidizing flame.

Quantitative Assay

A suitable quantity of the ore is dissolved in aqua regia, evaporated to dryness, and baked. The residue, when cold, is taken up with a little HCl, warmed until solution is effected, and diluted with water. Ammonia is now added until the solution is nearly neutral, and the Group II metals removed (together with the silica) by passing H_2S and filtering. The excess H_2S is boiled off and the iron oxidized with a few drops of HNO_3. Ammonia is added in slight excess, the solution boiled for a few minutes, and the precipitated iron filtered off after settling.

The filtrate from the iron is exactly neutralized with dilute H_2SO_4, methyl orange being used for indicator, about 5 drops of normal acid are added, and H_2S passed for half an hour. The solution is kept warm and allowed to stand and settle. The precipitate of ZnS is removed by filtering through paper pulp.

Co and Ni may now be precipitated by passing H_2S after the addition of ammonia, and the mixed sulphides are collected on a close paper, washed, and dissolved in aqua regia. The solution is made alkaline with ammonia in slight excess, warmed to about 80° C., and the Ni precipitated with an excess of 1-per-cent alcoholic solution of dimethylglyoxime. The precipitate is filtered through tared papers, washed well with hot water, and dried in the air-bath at 105° C. Factor: 0·2032.

COBALT, Co; atomic weight 58·97

THIS element is divalent, trivalent and tetravalent. Fused metallic cobalt is steel-grey in colour, is magnetic and has a specific gravity of 8·6 and a melting point of 1480° C. Cobaltous oxide, CoO, is a light-brown powder, and cobaltic oxide, Co_2O_3, very dark brown or brownish-black. Both oxides are soluble in hydrochloric acid. The ores of cobalt are generally found combined with arsenic and sulphur, and associated with nickel, copper and silver.

Smaltine, also known as *Tin-white Cobalt*. Cryst. system cubic, occurs massive, and reticulated (ret like). Colour, tin-white or steel-grey. Lustre metallic. Fracture uneven or granular. Hardness 5·5–6; specific gravity 6·4–7·2. A complex mineral of cobalt, nickel and iron arsenide, but usually considered as cobalt arsenide, $CoAs_2$: cobalt 28·2 per cent, arsenic 71·8 per cent. Found at St. Austell, Cornwall; Force Crag, near Keswick, Cumberland; Breeton, in Stirling; also in Saxony and Sweden, and the silver mines of South America.

Erythine or *Cobalt-bloom*. Cryst. system monoclinic, commonly found as oblique rhombic and rectangular prisms; occurs as incrustations, reniform and earthy. Colour, usually crimson-red, sometimes greenish. Hardness 1·5–2·5; specific gravity 2·95. Composition: a hydrated cobalt arsenate, $Co_3As_2O_3.8H_2O$. Cobalt oxide 37·55 per cent, arsenious oxide 38·43 per cent, water 24·02 per cent. Found in several Cornish mines; the old cobalt mine, Scar Crag, Cumberland, also Tynebottom mine near Alston in the same county. In several parts of Germany, Baden and Saxony; Norway, and in the state of Missouri, U.S.A.

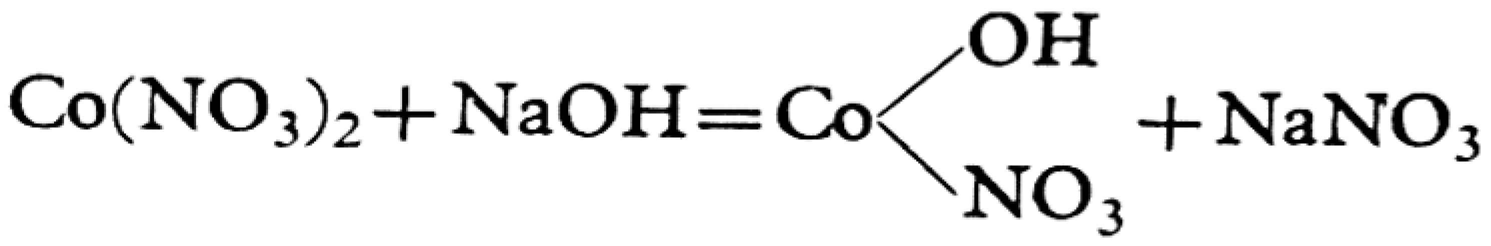
Cobaltine or *Cobalt-glance*. Cryst. system cubic. Colour, silver-white, sometimes having a reddish cast. Fracture uneven. Hardness 5·5; specific gravity 6·2. An arsenide and sulphide of cobalt, CoAsS: cobalt 35·5 per cent, arsenic 45·2 per cent, sulphur 19·3 per cent.

Earthy Cobalt or *Black Oxide of Cobalt.* Colour, blue-black. Condition amorphous; a complex mineral of cobalt, copper and manganese oxides $(CaOCuO)2MnO_2+4H_2O$. Very similar to wad, which has already been described under manganese. A manganese wad, which may have the manganese replaced by cobalt up to 36–38 per cent.

Qualitative Tests

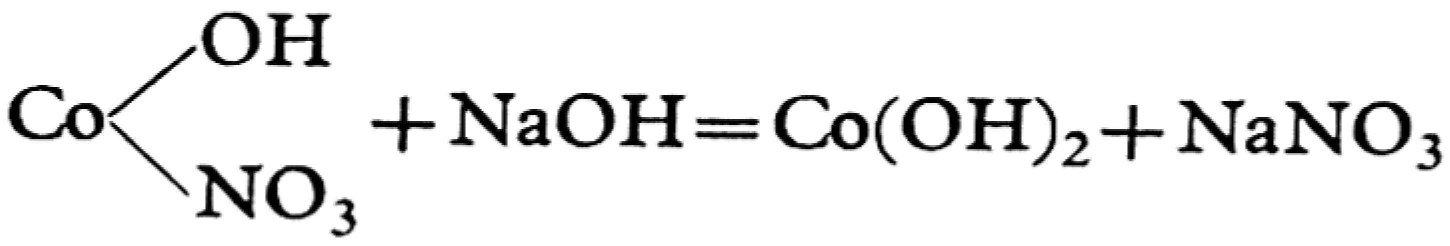
Salt used: cobalt nitrate, $(CoNO_3)_2.6H_2O$.

1. Sulphuretted hydrogen in the presence of hydrochloric acid gives no precipitate.
2. Ammonium sulphide causes a black precipitate of cobalt sulphide to form. Insoluble in acetic acid, and in dilute hydrochloric acid.
3. Sodium and potassium hydroxides, cause, in the first instance, a blue precipitate of a complex cobaltous salt to form, which, when boiled, gives a light-red cobaltous hydroxide. Later, further oxidation produces a brown cobaltic hydroxide. The change from blue to pinkish-red distinguishes cobalt from nickel:

(i) 

$$Co(NO_3)_2+NaOH=Co\!<\!\begin{matrix}OH\\NO_3\end{matrix}+NaNO_3$$

blue complex salt

(ii) 

$$Co\!<\!\begin{matrix}OH\\NO_3\end{matrix}+NaOH=Co(OH)_2+NaNO_3$$

light red cobaltous hydroxide

(iii) $2Co(OH)_2+O+H_2O=2Co(OH)_3$

brown cobaltic hydroxide

4. Ammonia causes a blue precipitate of complex salt to form, similar to sodium hydroxide, as given above; soluble in excess of the reagent.
5. Potassium cyanide causes a lightish-brown precipitate of cobaltous cyanide to form, which is soluble in excess, at first giving potassium cobaltocyanide, which on oxidation passes to potassium cobalticyanide:

(i) $CO(NO_3)_2+2KCN=Co(CN)_2+2KNO_3$

(ii) $Co(CN)_2+4KCN=K_4Co(CN)_6$

(iii) $2K_4Co(CN)_6+O+H_2O=2K_3Co(CN)_6+2KOH$

The potassium cobaltocyanide is analogous to potassium ferrocyanide and the potassium cobalticyanide to the ferricyanide.

6. Potassium nitrite and acetic acid form a yellow precipitate of potassium cobaltinitrite (Fischer's salt or cobalt yellow). This is used as a pigment by artists under the name of cobalt yellow or aureolin. Precipitation is assisted by the addition of potassium acetate and 80 per cent. alcohol. (See nickel.)

$$Co(NO_3)_2+7KNO_2+2CH_3COOH$$
$$=K_3Co(NO_2)_6+2CH_3COOK+2KNO_3+H_2O+NO$$

7. Nitroso-β-naphthol causes a voluminous purple-red precipitate of cobaltinitroso-β-naphthol, $C_{10}H_6O(NO)_3Co$, to form in solutions of cobaltous salts. The solution under test is acidified with hydrochloric acid and an equal volume of alcohol, and then gently warmed. To this is then added in fair excess a freshly prepared solution of nitroso-β-naphthol in 50-per-cent acetic acid, and the whole heated to boiling, resulting in the purple-red precipitate stated above.
8. Cobalt compounds, when heated on charcoal in the reducing flame, give a black powder, which is slightly magnetic.

With the borax bead, both the oxidizing flame and the reducing flame give a blue colour. With microcosmic salt the bead, with both the oxidizing flame and the reducing flame, is usually violet, sometimes blue. When iron is also present, both the blue and violet beads have a greenish cast, and in some cases may be strongly green when cold.

Quantitative Assay

This metal, which is precipitated as sulphide in ammoniacal solution, can be estimated as such or as Co_3O_4 after precipitation with nitroso-β-naphthol. In the former method, the combined sulphides of Co and Ni can be ignited and weighed, the residue dissolved in aqua regia, and the Ni estimated by precipitation with dimethylglyoxime (see nickel). The percentage of cobalt is taken by difference.

In the latter method the combined sulphides are dissolved in aqua regia, the solution is evaporated to a small bulk to remove excess acid, and then diluted with about 150 ml. warm water. A freshly prepared hot solution of nitroso-β-naphthol in 50-per-cent acetic acid is now added in excess, and the solution is left in a warm place for a few hours. The precipitate is filtered off and washed with cold water and 12-per-cent warm HCl alternately to remove any Ni (which can be estimated in the filtrate with dimethylglyoxime), gently ignited, and weighed as Co_3O_4.

URANIUM, U; atomic weight 238·07

THIS element is a greyish-white or a steel-white metal which oxidizes readily on heating strongly. It has a specific gravity of 18·68 and is most difficult to fuse. It is contained in pitchblende, a uranium oxide containing in addition small amounts of lead, silica and iron.

Samarskite, a complex mineral of iron, calcium and uranium, with minute quantities of erbium, cerium, niobium and tantalum, has a composition of $(FeCaUO_2)_3(UErCe)_2(NbTa)_6O_{21}$.

Pitchblende. Cryst. system cubic. Usually occurs massive or in spheroidal aggregations. Colour, black, greyish-black or brown. Hardness 5·5; specific gravity 6·4–6·8. Usually contains about 8–10 per cent of lead. Composition: uranious-uranic oxide, U_3O_4, 68–86 per cent.

Uraconite or *Uranic Ochre*. An earthy amorphous mineral. Colour, lemon-yellow to orange. A hydrated sulphate and uranic oxide: uranic oxide 60–70 per cent, sulphates, SO_3, 8–10 per cent, water 20 per cent. Occurs in various parts of the Cornish mining district, often in association with pitchblende.

Copper Uranite, $(CuO+2U_2O_3)P_2O_5+8H_2O$. Cryst. system tetragonal. Hardness 2–2·5; specific gravity 3·4–3·6. Composition: uranic oxide 59–61 per cent, phosphoric acid 14–16 per cent, copper oxide 8·5–9 per cent, water 14–15·5 per cent.

Calcium Uranite, $(CaO.3U_2O_3)P_2O_5.8H_2O$. Cryst. system rhombic. Hardness 2–2·5; specific gravity 3–3·2. Hydrated uranium phosphate and calcium hydrate: uranic oxide 56·5–61·0 per cent, phosphoric acid 13·5–15·2 per cent, lime (approx.) 5·5 per cent, water 15·5–20 per cent.

All these minerals are highly radioactive.

Qualitative Tests

COMPOUNDS AND SALTS OF TETRAVALENT URANIUM

1. Ammonium sulphide gives a light-green precipitate which turns black when boiled.
2. Potassium ferricyanide causes a yellowish-green precipitate to form, which, on standing, becomes darker by oxidation, changing to a reddish-brown.
3. Potassium ferrocyanide causes a reddish-brown precipitate to form.

COMPOUNDS AND SALTS OF HEXAVALENT TYPE

1. Ammonium sulphide in neutral solutions gives a chocolate-brown precipitate in the cold. This is soluble in excess of the reagent when this contains a little ammonium carbonate.
2. Potassium and sodium hydroxides cause a yellow precipitate (alkaline uranates) to form; insoluble in excess.
3. Hydrogen peroxide gives a yellowish-white or light-yellow precipitate of uranium tetroxide (UO_4); soluble in hydrochloric acid.

With the borax bead, a reddish-yellow bead is formed when heated in the oxidizing flame; colourless or faintly yellow when cold. In the reducing flame, a green bead is produced when hot, which is dark bottle-green when cold. With microcosmic salt, the oxidizing flame gives a yellow bead when hot, yellowish-green when cold; and the reducing flame yields a dirty green bead when hot and clear green when cold.

Note.—Uranium ores and compounds are most easily detected by their radioactive properties, the Geiger counter being commonly used for this purpose in prospecting work.

Quantitative Assay

Dissolve a suitable quantity of the ore in HNO_3 and take to fuming with H_2SO_4. When cold, take up with water and add excess of soda-ash solution. Bring to the boil and allow to settle. Filter off the insoluble matter, together with any metals precipitated as carbonates. Redissolve the precipitate in dilute H_2SO_4 and reprecipitate with soda-ash solution, adding the filtrate to the first and main filtrate.

Make the filtrate just acid with dilute H_2SO_4, add 10 ml. 10-per-cent ammonium-phosphate solution, bring to the boil, and add a slight excess of ammonia. The uranium is precipitated as uranium-ammonium phosphate.

Collect the precipitate on a close paper and wash with a dilute solution of ammonium sulphate and hot water. Redissolve the precipitate in dilute H_2SO_4, dilute to about 150–200 ml. and insert a sheet of aluminium in the beaker, bent in the form of a triangle for convenience (see copper assay). Boil gently on the hot plate for an hour, rinse and remove the aluminium, and titrate the hot solution with potassium-permanganate solution.

VANADIUM, V; atomic weight 50·95

Vanadium is a light-grey metal, sometimes silver-white. The specific gravity of vanadium is (approx.) 5·8, and the melting point, according to Ruff and Martin, 1715° C. Vanadium yields 4 oxides: vanadium dioxide, V_2O_2; trioxide, V_2O_3; tetroxide, V_2O_4 and pentoxide, V_2O_5. Vanadium enters into several useful alloys, such as ferrovanadium, used in making other alloys with steel. It has the property of imparting hardness and malleability to steel, and when added in small amounts also increases the tensile strength. Found in various rare minerals in conjunction with lead, zinc and aluminium, and also as a sulphide. One of the chief minerals is *Vanadinite*, $3Pb_3(VO_4)_2PbCl_2$; also *Desclorzite*, $PbZn_2(OH)VO_4$. The chief source of the former mineral is Russia, but it has also been found in the county of Cheshire, while the latter mineral is found in Mexico and in Chile, South America. Besides these, *Roscoelite*, a vanadium-aluminium silicate, and a native sulphide, are found in Peru.

Other ores of industrial importance are *Patronite*, an impure vanadium sulphide found in Peru, and *Carnotite*, a potassium uranyl vanadate, found in Utah and Colorado.

Qualitative Tests

1. Ammonium sulphide causes a brown precipitate of vanadium sulphide, V_2S_5, to form, which slowly dissolves in excess to a brownish-red solution.
2. In slightly acid solutions tannic acid causes a blue-black precipitate to form.
3. In both the oxidizing and reducing flames borax beads are colourless when cold, but when hot the oxidizing flame gives a yellow or orange bead, and in the reducing flame a green bead. With microcosmic salt vanadium compounds give a dark yellow bead when hot and a light yellow bead when cold, and with the reducing flame, a brownish bead when hot and emerald-green when cold.

Quantitative Assay

From 1 to 3 gram of the finely crushed ore is fused with about 8–10 gram of sodium peroxide in a nickel crucible. The melt is extracted with water, which is diluted and filtered, the precipitate being dissolved in H_2SO_4 and reprecipitated with ammonia if necessary.

The filtrate is acidified with dilute H_2SO_4, brought to the boil, and saturated with H_2S, allowed to settle, and the precipitate, containing molybdenum, removed by filtration. The filtrate is collected in a flask to which is fitted a bunsen valve, and the excess H_2S is removed by boiling—a little marble should be inserted to complete the expulsion of the gas, or else a similar arrangement to that used for tin assays could be adopted, the funnel being filled with soda-ash solution when the gas has been practically expelled. The hot solution is now titrated with standard potassium-permanganate solution, the vanadium, which had been reduced by the H_2S to V_2O_4, being oxidized to V_2O_5. As a check, the solution can be reduced again by passing through SO_2 from a syphon, the excess boiled off, and the solution again titrated with permanganate. The latter figure will be the more accurate.

BARIUM, Ba; atomic weight 137·37

METALLIC barium is a divalent yellowish-white metal; specific gravity 3·78–4·0, and melting point 850° C. approx. It readily oxidizes in the air, and has to be preserved under naphtha. When moistened with water it develops heat, forming barium hydroxide, $Ba(OH)_2$. The following are the most important minerals.

Barytes or *Heavy Spar*, $BaSO_4$. Cryst. system rhombic, usually found as modified rhombic prisms. Colour, white, sometimes colourless; also found yellowish-red or brown, due to iron compounds, which are usually removed by bleaching with acids. Lustre vitreous or resinous. Hardness 2·5–3·5; specific gravity 4·3–4·7. Composition: barium sulphate. The most frequently used " extender " in connection with paint manufacture. The following fine samples of Barytes gave: barium sulphate 95·22 per cent, 96·50 per cent, 97·92 per cent, 98·50 per cent, 98·90 per cent, the balance being made up of silica, iron oxide, alumina, magnesia and moisture. The last sample is from an English mine in Shropshire.

Witherite, $BaCO_3$. Cryst. system rhombic. Found massive; also as spheroidal aggregations or root-like shapes (tuberose). Colour, white, grey or yellowish-white. Lustre vitreous, sometimes resinous. Hardness 3–3·7; specific gravity 4·3–4·35. Composition, barium carbonate: baryta, BaO, 77·7 per cent, carbon dioxide, CO_2, 22·3 per cent.

Barytocalcite. Cryst. system monoclinic, usually found as oblique rhombic prisms. Colour, white, grey and yellowish-white. Lustre vitreous. Fracture uneven. Hardness 4; specific gravity 3·6. A double carbonate of calcium and barium. Formula, $BaCO_3+CaCO_3$, barium carbonate 66·3 per cent, calcium carbonate 33·7 per cent.

Qualitative Tests

Salt used: barium chloride, $BaCl_2.2H_2O$.

1. Potassium and sodium hydroxides, also ammonia, cause a white precipitate of barium hydroxide to form, but the formation of the precipitate will be prevented if ammonium chloride is present in a concentrated solution:
$$BaCl_2+2NH_4OH=Ba(OH)_2+2NH_4Cl$$
2. Sulphuric acid and all soluble sulphates cause a heavy white precipitate of barium sulphate to form; insoluble in ammonium acetate (distinction from lead sulphate), and also in boiling nitric acid:
$$BaCl_2+H_2SO_4=BaSO_4+2HCl$$
3. Ammonium carbonate causes a white precipitate of barium carbonate to form; soluble with evolution of carbon dioxide on the addition of acetic acid:
$$BaCl_2+(NH_4)_2CO_3=BaCO_3+2NH_4Cl$$
4. Potassium chromate causes a yellow precipitate of barium chromate to form; insoluble in acetic acid, but soluble in hydrochloric acid:
$$BaCl_2+K_2CrO_4=BaCrO_4+2KCl$$
5. Ammonium oxalate gives a white precipitate of barium oxalate which does not readily form if acetic acid is present:
$$BaCl_2+(NH_4)_2C_2O_4=BaC_2O_4+2NH_4Cl$$
6. With the bunsen flame barium gives an apple-green colour.

Quantitative Assay

The sulphate of this metal being completely insoluble in water, advantage of this fact is taken in its estimation. In most ores containing the metal a quantity of it exists as barium sulphate, so that it is always necessary to fuse the insoluble matter with alkali carbonates. The fused mass is extracted with water and the insoluble barium carbonate filtered off, dissolved in HCl, and added to the main bulk.

A suitable quantity of the ore is dissolved in HCl and the insoluble matter filtered off. It is preferable to evaporate to dryness and bake as in the estimation of silica. If lead is present the solution must be nearly neutralized with ammonia and gassed with H_2S, the precipitated lead sulphide being removed by filtration. After boiling to remove the excess of H_2S, a little 50-per-cent H_2SO_4 is added and the solution boiled for a further 10 minutes or so, and allowed to settle, preferably overnight. The precipitate is collected on a No. 42 or 32 Whatman paper, washed well with hot water and very dilute HCl (about 20 ml. of the strong solution in 500 ml. hot water), ignited, and weighed. $BaSO_4$ contains 0·5885 gr. Ba/gr.

When free from lead, iron and zinc, barium may be precipitated from a neutral solution with potassium bichromate, the precipitate being collected and washed well with hot water, dissolved in normal HCl, and the chromic acid estimated with thiosulphate (see thiosulphate estimation of lead).

STRONTIUM, Sr; atomic weight 87·63

THIS element is divalent, the metal being white with a yellowish cast. It has a specific gravity of 2·50–2·57, and has a melting point of about 800° C. The two chief minerals are celestine and strontianite.

Celestine. Cryst. system rhombic, usually found as modified rhombic prisms; also occurs massive, granular and sometimes fibrous. Colour, white. Lustre vitreous. Hardness 3–3·5; specific gravity 3·9. Composition (strontium sulphate): strontium oxide, SrO, 56·40 per cent, sulphur trioxide 43·6 per cent. Formula $SrSO_4$.

Strontianite. Cryst. system rhombic, usually found as modified rhombic prisms; also found granular and fibrous. Colour, white when pure, but also found off-colour white, grey, yellowish-white and pale-green. Lustre vitreous. Specific gravity 3·6–3·7. Insoluble in water, but soluble in dilute acids. Composition, strontium carbonate: strontium oxide, SrO, 70·10 per cent; carbon dioxide, CO_2, 29·90 per cent. Formula $SrCO_3$.

Qualitative Tests

Salt used: strontium chloride $SrCl_2$.

1. Potassium and sodium hydroxides, also ammonia, cause a white precipitate of strontium hydroxide to form. Should ammonium chloride be present the precipitate will not be produced, and in any case the solution must be fairly concentrated:

$$SrCl_2 + 2NH_4OH = Sr(OH)_2 + 2NH_4Cl$$

2. Ammonium carbonate causes a white precipitate of strontium carbonate to form; soluble in dilute acetic acid:

$$SrCl_2+(NH_4)_2CO_3=SrCO_3+2NH_4Cl$$

3. Sulphuric acid and soluble sulphates cause a white precipitate of strontium sulphate to form. It is insoluble in a strong boiling solution of ammonium sulphate which has been made alkaline by ammonia (distinction from calcium sulphate):

$$SrCl_2+H_2SO_4=SrSO_4+2HCl$$

   In order to obtain complete precipitation, the solution should be allowed to stand for a short time on the hot plate.
4. Ammonium sulphide gives no precipitate.
5. Potassium chromate gives no precipitate in dilute solutions at first, but only on standing some time, and then produces a light-yellow precipitate. In highly concentrated solutions the precipitate comes down almost at once, being easily soluble in acetic acid:

$$SrCl_2+K_2CrO_4=SrCrO_4+2KCl$$

6. Ammonium oxalate causes a white precipitate of strontium oxalate to form; soluble in hydrochloric and nitric acids, but only slightly soluble in acetic acid:

$$SrCl_2+(NH_4)_2C_2O_4=SrC_2O_4+2NH_4Cl$$

7. In the bunsen flame strontium compounds give a crimson flame.

Quantitative Assays

Assay as strontium carbonate.

The carbonate is precipitated by the addition of ammonium carbonate in slight excess to a solution which has been made ammoniacal and then heated nearly to boiling. It is then removed from the source of heat and allowed to cool and stand for 12 hours, preferably all night, then filtered cold and washed. The precipitate is then transferred to a previously weighed silica or platinum crucible. The filter paper is ignited separately and the ash added to the crucible, and the whole gently ignited, cooled and weighed:

$$SrCO_3\times 0{\cdot}7010=SrO \text{ or } \times 0{\cdot}5935=Sr$$

Strontium can also be precipitated as oxalate by adding ammonium oxalate to a slightly ammoniacal solution. The precipitate is filtered and well washed with distilled water containing about 1 gram of ammonium oxalate per 1000 ml. The precipitate is best filtered into a Gooch silica crucible having a prepared asbestos plug, which has been carefully weighed prior to being used. The precipitate is then ignited and weighed as SrO:

$$SrO\times 1{\cdot}7726=SrSO_4 \text{ or } \times 1{\cdot}4247=SrCO_3$$

CALCIUM, Ca; atomic weight 40·07

THIS element is a divalent yellowish-white metal; specific gravity 1·52 and melts at 810° C. It is very easily oxidized. Calcium is very abundant in nature in limestone, chalk, gypsum, dolomite, apatite.

Calcite, $CaCO_3$. Cryst. system hexagonal. Found as hexagonal prisms, rhombohedral, stalactitic, fibrous and granular. Colour, when pure, white, but often coloured by small amounts of other elements, being then found yellow, red or rose coloured. Lustre vitreous, sometimes earthy. Hardness 2·5–3·5; specific gravity 2·6–2·7. Composition, $CaCO_3$: calcium oxide, CaO, 56 per cent, carbon dioxide 44 per cent. A good calcite will consist of calcium carbonate 99·82 per cent, the balance being made up of silica and alumina.

Limestone (calcium carbonate) occurs in extensive deposits which, as mountain limestone, extend from the Weaver Hills in Staffordshire right up to the Scottish border. Dolomite limestone, $CaMg(CO_3)_2$, or dolomite, is found extending from Nottingham across England to Tynemouth.

Dolomite. Cryst. system rhombohedral, occurring in rhombohedra with the faces frequently curved. It also occurs massive, and sometimes granular as a very solid crystalline rock. An average sample may contain 54 per cent of calcium carbonate, 41·5 per cent magnesium carbonate, and the balance of 4·5 per cent, chiefly silica and small amounts of alumina, iron oxide and organic matter. Hardness 3·5–4·0; specific gravity 2·8–2·9.

Gypsum. Cryst. system monoclinic. A crystalline variety is known as *Selenite*, while a fibrous variety is known as *Satin-spar*. The colour of gypsum, when pure, is white, but is frequently contaminated with traces of iron compounds, giving a yellowish, red or brown colour. Hardness 1·5–2; specific gravity 2·3. The percentage of calcium sulphate, $CaSO_4$, may vary from about 60 per cent to 79·5 per cent, and the amount of water from 17 per cent to 21 per cent, the balance consisting of small amounts of silica, alumina, iron oxide, lime and magnesia. Some gypsums may contain as much as 13 per cent $CaCO_3$ and 16 per cent of SiO_2. Formula $CaSO_4.2H_2O$.

Aragonite. Cryst. system rhombic. Very often found twinned on the faces of the prisms, which are compound six-sided ones. Colour, white, yellowish-white, greenish or grey. Lustre vitreous. Fracture subconchoidal. Hardness 3·5–4; specific gravity 2·93. Composition: calcium carbonate, $CaCO_3$.

Apatite. Cryst. system hexagonal, common form hexagonal prisms.

Colour, pale green or yellowish-green or yellow. May also be found bluish-green, light blue, grey, reddish-brown and occasionally white. Lustre vitreous or subresinous. Hardness 4·5–5·0; specific gravity 2·9–3·25. Composition, calcium fluophosphate, $3Ca_3P_2O_8.CaF_2$: calcium oxide 55·5 per cent, phosphoric acid 42·3 per cent, fluorine 3·8 per cent. Another variety replaces the fluorine by chlorine, consisting of calcium oxide 52·27 per cent, phosphoric acid 40·92 per cent and chlorine 6·81 per cent. $3Ca_3P_2O_8.CaCl_2$.

Anhydrite. Cryst. system rhombic. Usually found as prisms, either right rhombic or right rectangular in shape, or as combinations of the two. May also occur lamellar or plate-like, fibrous and granular. Colour, white; also greyish white and reddish-white, and occasionally it is tinted blue. Fracture uneven. Hardness 3–3·5; specific gravity 2·8–2·9. Composition, calcium sulphate, $CaSO_4$: calcium oxide 41·2 per cent, sulphur trioxide 58·8 per cent. Found associated with rock salt in the Stassfurt potash mines and at Billingham, Co. Durham.

Fluorspar or *Blue John Spar.* Cryst. system cubic. Found near Matlock and known as *Derbyshire Blue John Spar*; in various colours, such as purple, amethyst, blue-green, white and colourless. Lustre vitreous. Hardness 4; specific gravity 3–3·25. Composition, calcium fluoride, CaF_2: calcium 51·3 per cent, fluorine 48·7 per cent. The purple and amethyst shades are due to the presence of manganese.

Qualitative Tests

Salt used: calcium chloride, $CaCl_2$.

1. Potassium and sodium hydroxides, also ammonia, give, in concentrated solutions and when free from excess of ammonium chloride, a white precipitate of calcium hydroxide:

$$CaCl_2+2NH_4OH=Ca(OH)_2+2NH_4Cl$$

2. Ammonium carbonate causes a white precipitate of calcium carbonate to form, which, on being left on the hot plate, settles out rapidly. Soluble in acetic acid:

$$CaCl_2+(NH_4)_2CO_3=CaCO_3+2NH_4Cl$$

3. Ammonium sulphide gives no precipitate.
4. Sulphuric acid, in concentrated solutions, gives a white precipitate of calcium sulphate which will form slowly, but does not form in weak or dilute solutions. The precipitate dissolves completely if much water is added, and is quite soluble in dilute acids:

$$CaCl_2+H_2SO_4=CaSO_4+2HCl$$

5. Ammonium oxalate causes a white precipitate of calcium oxalate to form. Insoluble in acetic acid, but soluble in hydrochloric acid:

$$CaCl_2+(NH_4)_2C_2O_4=CaC_2O_4+2NH_4Cl$$

6. Flame test in bunsen with platinum wire, dark red. Powdered anhydrite, when fused with sodium carbonate, gives a mass which, when placed on a silver coin and moistened, causes a black stain.

Quantitative Assay

A fairly rapid method for the estimation of calcium is based on the conversion of the oxalate to sulphate and the titration of the freed oxalic acid with permanganate. A portion of the material is dissolved in HCl, diluted with water, nearly neutralized with ammonia, and saturated with H_2S. After standing warm to settle, the Group II metals are filtered off and the filtrate boiled to expel the excess gas. When free from H_2S a few drops of HNO_3 are added to oxidize the iron, which is then precipitated with ammonia and removed. To the boiling filtrate 10 ml. of 10-per-cent ammonium oxalate is added, the solution boiled for a further 10 minutes, and allowed to settle in a warm place. The precipitate is collected on a No. 30 or 40 Whatman paper, dissolved in HCl, and reprecipitated with ammonia and ammonium oxalate.

The precipitate is again filtered, washed well with hot water, and then washed back into the original beaker, the paper being washed with hot 10-per-cent H_2SO_4. The free oxalic acid is now titrated with N/10 potassium-permanganate solution. 1 ml. equals 2 mg. Ca.

MAGNESIUM, Mg; atomic weight 24·32

THIS element is divalent. It is a hard silver-white malleable metal, having a specific gravity of 1·743 and melting at 633° C.–650° C., and when heated in the air burns with a very dazzling white light, giving off white fumes of magnesium oxide. The metal dissolves easily in dilute hydrochloric acid.

Apart from occurring in magnesium limestone (dolomite), which has already been mentioned under calcium, it occurs as many other minerals, such as magnesite, brucite and epsomite.

Magnesite. Cryst. system rhombohedral. It is usually a compact massive rock, showing in some cases a fibrous structure, but is occasionally found granular. When pure the colour is white, but the presence of small amounts of impurities produces yellowish-white, greyish-white and light-brown specimens. Hardness 3·5–4·5; specific gravity, when crystalline, 3; when granular, 2·8–3. Composition, magnesium carbonate, $MgCO_3$: magnesia, MgO, 47·6 per cent, carbon dioxide 52·4 per cent.

Brucite. Cryst. system hexagonal and rhombohedral. Usually found as hexagonal prisms. Occurs massive and sometimes fibrous. Colour, white, greyish-white and greenish-white. Hardness 2·5; specific gravity 2·3. Composition, magnesium hydrate: magnesium oxide, MgO, 69 per cent, water 31·0 per cent.

Epsomite. Cryst. system rhombic. Colour, white. Lustre vitreous. Has a bitter saline taste. Composition, hydrated magnesium sulphate $MgSO_4.7H_2O$: magnesium oxide 16·36 per cent, sulphur trioxide 32·48 per cent, water 51·16 per cent.

For *Serpentine* and *Chrysotile*, $3MgO.2SiO_2.2H_2O$, see Silicates; and for *Carnallite*, $MgCl_2.KCl.6H_2O$, see Potassium.

Qualitative Tests

Salt used: magnesium sulphate, $MgSO_4.7H_2O$.

1. Potassium and sodium hydroxides, also ammonia, cause a white precipitate of magnesium hydroxide to form; insoluble in excess, but soluble in the presence of ammonium salts, such as ammonium chloride:

$$MgSO_4+2NH_4OH=Mg(OH)_2+(NH_4)_2SO_4$$

2. Ammonium carbonate causes a white precipitate of magnesium carbonate to form slowly with concentrated solutions, but this is dissolved by ammonium chloride:

$$MgSO_4+(NH_4)_2CO_3=MgCO_3+(NH_4)_2SO_4$$

3. Sodium phosphate, Na_2HPO_4, causes a white precipitate of magnesium phosphate to form, which is soluble in acids:

$$MgSO_4+Na_2HPO_4=MgHPO_4+Na_2SO_4$$

4. Sodium phosphate, in conjunction with ammonia, gives a white precipitate of magnesium ammonium phosphate:

$$MgSO_4+NH_4OH+Na_2HPO_4=MgNH_4PO_4+Na_2SO_4$$

Quantitative Assay

Magnesium is estimated gravimetrically as magnesium pyrophosphate, which is precipitated in ammoniacal solution after the removal of the heavy metals by group separation. For the analysis of raw or burnt magnesite the following procedure should be adopted.

Weigh into a 400-ml. squat beaker 5 gram of the dried sample, add 20 ml. HCl, and warm until dissolved. When solution is complete remove cover-glass and evaporate carefully to dryness, baking for half an hour to render the silica insoluble. Cool, add 10 ml. HCl, warm until redissolved, dilute to about 40 ml., and filter. To obtain the percentage of carbonaceous matter in the insoluble part it is best to use tared papers for filtering* in the following way:

Take two papers (Nos. 40 or 30 Whatman are suitable) from the middle of a box—which, lying together, should contain a similar amount of moisture—fold and place one on each pan of the balance. Theoretically the papers should be dried in the air-bath before weighing, but this practice always renders them brittle and liable to crack while in use. On the other hand, since the moisture content of each paper must be very low, it follows that for all practical purposes the *difference* in the moisture can be neglected. Swing the balance, and place the heavier paper on the right-hand pan. Cut small pieces from the edge of the folded heavier paper until the papers are exactly the same weight, fold the two papers together, the cut one on the outside, and place in the funnel.

After filtering off the silica, wash three or four times with hot water, place the funnel over a fresh beaker, and continue the washing until the filter is shown to be entirely free from acid, a few ml. of silver-nitrate solution contained in a test tube being held underneath the funnel periodically until no precipitate of AgCl is formed. The filter and contents are now dried at 100° C. in the water or air-bath, cooled in the desiccator, and weighed, the cut filter being used as a tare on the right-hand pan of the balance. The paper containing the insoluble matter is now ignited in a porcelain or silica crucible. The residue should be silica, and the difference in weight between the total insoluble matter and the residue after ignition is the carbonaceous matter.

To the filtrate from the silica, add a few drops of HNO_3 to oxidize the iron, then add a little ammonia, precipitating the iron and alumina together. Bring to the boil and stand hot to remove excess ammonia, and allow to settle. Filter, wash twice with hot water, and redissolve in dilute HCl. Precipitate again with ammonia, remove excess, and filter, adding filtrate to the first portion. The filter can be ignited and weighed, the iron estimated with potassium bichromate or colorimetrically with potassium or ammonium thiocyanate, converted to Fe_2O_3, and alumina taken by difference.

To the boiling filtrate from the iron and alumina add 10 ml. of strong ammonium-oxalate solution, boil for 10 minutes, and allow to settle. Filter and wash with hot water, dissolve precipitate in HCl, add excess ammonia and boil. Add a further 10 ml. ammonium oxalate, boil for 10 minutes, and settle. Filter, collecting filtrate in original beaker. The lime is now estimated volumetrically with potassium permanganate in the usual way, while the filtrates from it are cooled and made up to 1 litre, and well mixed.

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* In the gravimetric method a preferable alternative to the use of tared papers is the sintered glass crucible, grade G.3 or G.4.

From this solution pipette out 100 ml. into a 600-ml. beaker (equivalent to 0·5 gram of the sample), dilute to about 300 ml. with distilled water, and make just alkaline with ammonia. Bring to the boil, and, while still boiling, add a large excess of ammonium-phosphate solution; continue to boil for 10 minutes, and allow to cool. When somewhat cooler add a large excess of ammonia and stir vigorously. Stir periodically for about 2 hours and allow to settle, preferably overnight. Filter, washing with water and dilute ammonia, ignite, and weigh as $Mg_2P_2P_7$. Factor: 0·2184.

In the case of ores containing zinc, it will be necessary to remove this metal, which is also precipitated with ammonium phosphate. The Group II metals having been separated with hydrogen sulphide, the filtrate is oxidized and the iron and alumina precipitated with ammonia. To the filtrate from this separation a few drops of methyl orange are added, and then dilute H_2SO_4 until the solution is just neutral. A strong current of hydrogen sulphide is now passed for an hour, the precipitate allowed to settle, and filtered off through paper pulp. H_2S is again passed through the filtrate to ensure that no further zinc is present. After boiling to remove excess H_2S, the lime is precipitated, after which the magnesium is determined in the usual manner.

POTASSIUM, K (Kalium); atomic weight 39·1

Potassium is a soft silver-white metal which is instantly oxidized in the air. The specific gravity is 0·8629 at 0° C., and the melting point is 62·5° C. Potassium is monovalent, and decomposes water into hydrogen and potassium hydroxide. The element is found in nature as nitre, or potassium nitrate, and in several minerals in the potash deposits of Stassfurt in Germany, and the Dead Sea, of which carnallite, kieserite and kainite are the most important.

The *Stassfurt Deposits*, discovered in 1839, have in the past provided a large proportion of the potassium salts of commerce, in addition to sodium and magnesium salts. The following minerals are found in the deposits:

Mineral	*Empirical Formula*
Sylvine	KCl
Carnallite	$KCl.MgCl_2.6H_2O$
Douglasite	$2KCl.FeCl_2.2H_2O$
Polyhalite	$K_2SO_4.MgSO_4.2CaSO_4.2H_2O$
Kainite	$K_2SO_4.MgSO_4.MgCl_2.6H_2O$
Schönite	$K_2SO_4.MgSO_4.6H_2O$
Krugite	$K_2SO_4.MgSO_4.4CaSO_4.2H_2O$
Rock-salt	$NaCl$
Glauberite	$Na_2SO_4.CaSO_4$
Astrakanite	$Na_2SO_4.MgSO_4.4H_2O$
Bishofite	$MgCl_2.6H_2O$
Boracite	$2Mg_3B_8O_{15}.MgCl_2$
Pinnoite	$MgB_2O_4.3H_2O$
Kieserite	$MgSO_4.H_2O$
Reichardite (Epsom Salts)	$MgSO_4.7H_2O$
Anhydrite	$CaSO_4$
Gypsum	$CaSO_4.2H_2O$
Tachhydrite	$CaCl_2.2MgCl_2.12H_2O$
Hydroboracite	$CaB_2O_4.MgB_2O_4.6H_2O$

Carnallite is a red-coloured mineral, due to the presence of ferric oxide; specific gravity, 1·6; hardness, 1. It has a conchoidal fracture, a greasy shiny lustre, intumesces when heated and is readily soluble in water.

Kainite is a colourless, grey or yellow mineral, with a vitreous lustre and is readily soluble in water: specific gravity 2·13; hardness 2.

Kieserite is white, grey or yellow, with a vitreous lustre, readily fusible and soluble in water: specifiic gravity 2·5; hardness 3.

Sylvine. Cryst. system cubic. Colour, white, sometimes found colourless. Hardness 2; specific gravity 1·9–2·0. Composition, potassium chloride, KCl: potassium 52·5 per cent, chlorine 47·5 per cent.

Nitre. Potassium nitrate or saltpetre. Cryst. system rhombic. Colour, white. Lustre vitreous. Hardness 2; specific gravity 1·93. Composition, potassium nitrate, KNO_3: K_2O 46·58 per cent, N_2O_5 53·42 per cent.

Qualitative Tests

Salt used: potassium nitrate, KNO_3, or chloride, KCl.

1. Chloroplatinic acid, H_2PtCl_6. This test is best carried out on a

watch glass, and, since potassium chloroplatinate is insoluble in alcohol, its formation is much assisted by the addition of a little absolute alcohol, and stirring well with a glass rod. With concentrated solutions, the yellow precipitate of potassium chloroplatinate comes down at once, as a precipitate of octahedral crystals. If the solution of the potassium salt is alkaline, it must be saturated with hydrochloric acid before adding the chloroplatinic acid. If large amounts of sodium salts are present, the sensitiveness of the reaction is affected:

$$2KNO_3+H_3PtCl_6=K_2PtCl_6+2HNO_3$$

2. Tartaric acid and sodium hydrogen tartrate give a white precipitate with potassium salts of potassium hydrogen tartrate, $KHC_4H_4O_6$, which comes down rapidly with strong solutions, but much more slowly in dilute ones. Shaking or rapid stirring with a glass rod promotes the formation of the precipitate. The precipitate is dissolved by mineral acids and alkalies and is soluble in hot water:

$$KCl+NaHC_4H_4O_6=KHC_4H_4O_6+NaCl$$

3. Perchloric acid, $HClO_4$, produces in acid, alkaline or neutral solutions of potassium salts, a white crystalline precipitate of potassium perchlorate, $KClO_4$, which is only slightly soluble in acids and alkalies (hydroxide) solutions. Ammonia salts give no reaction with perchloric acids:

$$KCl+HClO_4=KClO_4+HCl$$

SODIUM, Na (Natrium); atomic weight 23·00

SODIUM is a monovalent metal, melting point 97·5° C., boiling point 750° C. When unoxidized it is a bright, silvery metal, but on exposure to moist air is rapidly covered with a film of hydroxide and it is therefore stored under paraffin. Sodium is one of the most abundant of the earth's elements, though the metal does not exist naturally in the free state. Minerals based on sodium include:

Rock-salt, sodium chloride, NaCl. This is the most abundant natural mineral containing sodium, being the chief salt present in the sea and also occurring as rock-salt in very large deposits in many parts of the world. Rock-salt has a specific gravity of 2·1–2·2 and a hardness of 2. Crystal form, refular.

Chile Saltpetre, $NaNO_3$, as its name implies, occurs in Chile, in the districts of Atacama and Tarapaca.

Albite, $Na_2Al_2Si_6O_{16}$, is a sodium-aluminium silicate crystallizing in the triclinic system: specific gravity 2·6, hardness 6–6·5.

Cryolite, $6NaF.Al_2O_3$, has already been mentioned under aluminium.

Boronatrocalcite or *Ulexite*, $Na_2B_4O_7.CaB_4O_7.18H_2O$, and *Tincal*, or crude sodium borate, $Na_2B_4O_7.10H_2O$, are the principal sources of the borax and boric acid of commerce. Principal deposits are in Thibet, California and Chile.

Thenardite, sodium sulphate, Na_2SO_4, occurs in the anhydrous condition in Chile and Spain, whilst extensive deposits of the hydrated sulphates of sodium and calcium, *Glauberite*, occur in Spain and in the Stassfurt deposits. Sodium carbonate occurs in many inland lakes, such as Lake Magadi, the Great Salt Lake of Utah and the Dead Sea, whilst there are enormous deposits of carbonates, sometimes mixed with sulphate and chloride in California, Nevada and Wyoming. It also exists as incrustations in the soil of Egypt. In this form it is called *Trona*, and has the approximate composition $Na_2CO_3.NaHCO_3.2H_2O$.

Analysis. Sodium is estimated with potassium as the mixed alkali chloride. The separation of the alkali chlorides is described below.

Quantitative Assay

The term " Alkalies " is generally considered to mean sodium and potassium only, and the following method for their estimation can be employed.

Take 0·5–1 gram of the finely powdered mineral and mix with an equal weight of ammonium chloride. Add about eight times as much alkali-free calcium carbonate, mix thoroughly in a mortar, using part of the chalk to rinse out, and transfer the mixture to a platinum crucible. Heat the crucible gently for about 10 minutes with a bunsen burner, until the ammonium chloride is decomposed, then raise to red heat for about three-quarters of an hour, keeping the crucible covered. Cool and turn out the mass into a 4-inch evaporating dish, washing crucible and lid with distilled water and collecting the rinsings in the dish. Dilute to 60 or 80 ml., heat to boiling, filter and wash. Add to the filtrate about 1·5 gram of ammonium carbonate, evaporate to about 40 ml., and add a little more ammonium carbonate, and ammonia. Filter, collecting the filtrate in a squat beaker, evaporate to a low level and transfer to a tared platinum dish. When dry, gently ignite, and weigh the residue as KCl plus NaCl.

An alternative method is frequently used, the potassium being estimated by the platinic chloride method or by perchloric acid. The method is as follows: The solution, from which all other substances have been removed (by H_2S, ammonia, ammonium sulphide, ammonium oxalate and ammonium phosphate), is evaporated to dryness and ignited gently to remove ammonium salts. It is then treated with HCl, again ignited and the alkalies weighed as chlorides. If sulphuric acid or phosphoric acid is present, the substance is dissolved in a little water, and lead-acetate solution added, in slight excess, in the presence of alcohol. The lead is removed with sulphuretted hydrogen and the filtrate evaporated as before.

For the estimation of potassium by platinic chloride proceed as follows: The residue of mixed chlorides, which has been weighed, is now dissolved in a small quantity of hot water and filtered, and the filtrate, if clear, is treated with hydrochloric acid in slight excess, evaporated to dryness and gently ignited. The residue is now dissolved in a small amount of water, platinum tetrachloride added, and a drop or two of hydrochloric acid, and the whole evaporated nearly to dryness on the water bath. Should the solution loose its orange tint during evaporation more of the platinic salt must be added.

The moist residue is now treated with 80-per-cent alcohol, and then filtered into a previously weighed Gooch crucible, containing a plug of filter-paper pulp, and washed with alcohol until the washings are colourless. The precipitate and Gooch crucible are then dried, cooled and weighed, and the potassium chloroplatinate, K_2PtCl_6, calculated to K_2O. The factors are:

$$\begin{aligned} K_2PtCl_6 \times 0{\cdot}1938 &= K_2O \\ K_2PtCl_6 \times 0{\cdot}16085 &= K_2 \\ K_2PtCl_6 \times 0{\cdot}3584 &= K_2SO_4 \\ K_2PtCl_6 \times 0{\cdot}3067 &= 2KCl \end{aligned}$$

The percentage of potassium chloride found is then deducted from the mixed alkaline chloride previously determined, and the sodium is calculated from the difference.

The second method, using perchloric acid, is carried out as follows: The residue, after all other metals have been removed, is treated with hydrochloric acid, and again evaporated to dryness, and then gently ignited to remove ammonium salts, distilled water added, and evaporated in a porcelain dish to about 20 ml. To the solution thus prepared 12 ml. of a 10-per-cent solution of perchloric acid is added, and the whole evaporated on the water-bath, stirring to a syrupy consistency. A little more water is now added and again evaporated till abundant white fumes of perchloric acid are evolved. Now cool and add 25 ml. of 95-per-cent alcohol in which 1 ml. of perchloric acid solution has been added, mix thoroughly with a glass rod and allow to settle. After standing a short time pour off the top liquid into a previously weighed Gooch crucible fitted with a prepared asbestos plug. Now treat the residue in the evaporating dish twice by decantation with 25 ml. of the perchloric-alcohol, wash, finally transferring the precipitate to the Gooch crucible and washing with 25 ml. of the alcohol, and, finally, one wash with 95-per-cent alcohol. The crucible is now placed in the steam oven for two hours at 105° C., then cooled in the desiccator and weighed as $KClO_4$. The percentage may be reported as K_2O or K. The factor in the former case is obtained from the fraction $\frac{K_2O}{KClO_4} = \times 0{\cdot}3401$, and the other in a similar manner, $\frac{K}{KClO_4} = \times 0{\cdot}381$.

QUANTITATIVE ESTIMATION

of

ACIDIC RADICALS

CHLORINE

Determination in Neutral Salts. A suitable quantity of the material is dissolved in water in a 400-ml. conical flask or beaker and a drop or two of saturated potassium-chromate solution is added. Standard silver-nitrate solution is now run in from a burette until a red coloration of silver chromate appears.

Determination in Insoluble Salts or Ores. The material is weighed into a squat beaker and treated with dilute HNO_3. After boiling for a few minutes the solution is filtered through a close paper, the filtrate collected in a conical beaker or flask, and the paper washed with hot water in the usual way. The filtrate is now cooled and treated with 20 ml. of standard silver-nitrate solution and 5 ml. saturated (chlorine-free) iron-alum solution. The excess silver nitrate is now titrated with a solution of ammonium or potassium thiocyanate, the excess being shown by the red coloration of the ferric salt present. For convenience it is as well to adjust the strength of the thiocyanate solution so that 1 ml. of it is exactly equivalent to 1 ml. of the silver nitrate.

If silver is present in the material, the chloride of this metal will not dissolve in the HNO_3, so that the insoluble matter after washing with hot water must be treated with ammonia solution. The extract is now acidulated with HCl, and the AgCl collected on tared papers, dried, and weighed.

Available Chlorine. This term implies the amount of free chlorine which can be made to unite with hydrogen in water, throwing out the oxygen, and is used for the evaluation of bleaching powder and similar materials. A suitable method for the estimation of available chlorine in bleaching powder can also be used for the direct estimation of the strength of chlorine water, the procedure being as follows:

A suitable quantity of the water or solution of the powder is placed in a conical beaker or flask, diluted somewhat if necessary, and about 3 gram of potassium iodide is added, together with a few millilitres of freshly prepared starch-paste solution. For every atom of available chlorine present one atom of iodine will be released, which can be estimated in the usual manner with standard sodium-thiosulphate solution.

PHOSPHORUS

Quite the most satisfactory method for the estimation of phosphorus salts is by precipitation as ammonium phosphomolybdate, which contains 1·65 per cent P.

A convenient quantity of the finely divided mineral is weighed into a 250-ml. squat beaker and dissolved in HNO_3, with the addition if necessary of HCl. After solution is complete the cover-glass is rinsed in and removed, and the solution is allowed to go to dryness on the hot plate and is baked for an hour. The beaker is cooled, the residue taken up with a little HCl, warmed to complete solution, and the insoluble matter, after diluting somewhat, removed by filtration. (It is usual to estimate SiO_2 and phosphorus from the same trial.) The iron is now precipitated by the addition of ammonia, and contains the phosphorus. In the case of manganese ores or ores containing considerable quantities of manganese, it is advisable to precipitate the Fe as " basic acetate " in order to keep out manganese. The ferric hydrate or acetate is collected on an open paper, washed with hot water, and redissolved in HNO_3. A drop or two of SO_2 water will assist solution if necessary. It as as well to reprecipitate the Fe with ammonia, filter, and dissolve again in HNO_3 to remove traces of chlorine. The solution containing the iron is treated with a slight excess of ammonia, and then 10 ml. of 10-per-cent ammonium-molybdate solution, followed by 10 ml. strong HNO_3, which will redissolve the iron, precipitating the phosphorus at the same time.

Many assayers add the molybdate solution to the acid-iron solution, but the above method is to be preferred, the precipitate settling much faster. The beaker is agitated for a few minutes, or stirred with a " policeman," and then stood in a warm place (the top of the air-bath is suitable) to settle.

After standing at least an hour, the precipitate is filtered through a weighed sintered glass crucible, washed with 2-per-cent HNO_3, and dried in the air-bath at 105° C. Factor: 0·0165.

In the case of iron ores, it may be found that at least 5 gram of the sample must be taken to obtain a satisfactory figure, yet to filter such a large quantity of ferric hydrate as would be contained in that amount would be extremely difficult and tedious. This difficulty may be overcome in the following way:

To the filtrate from the insoluble matter add saturated SO_2 water, or pass the gas from a syphon, until the solution is practically colourless. Boil off the excess SO_2 and add ammonia in excess, and then acetic acid. A portion of the iron which is in the ferric state will be precipitated and will contain all the phosphorus; all the ferrous iron will remain in solution and can be removed by filtration. The precipitate is dissolved in HNO_3 and the assay continued in the above manner.

SILICA

Silica is to be found associated with almost every mineral and is practically insoluble in the common acids, with the exception of hydrofluoric acid. The general procedure for its estimation is as follows:

1 or 2 gram of the finely ground ore is weighed into a 250-ml. squat beaker and treated with about 20 ml. of HCl or aqua regia, according to the nature of the mineral. When solution is effected the cover-glass is rinsed in and removed and the solution allowed to evaporate slowly to dryness. When quite dry, the beaker is transferred to the centre of the hot-plate and baked for half an hour. After cooling, the residue is taken up with about 5 ml. HCl and a few millilitres of hot water, brought to the boil, and, after settling, filtered through a close paper, washed well with hot water and dilute HCl, and ignited in a platinum crucible. For the preservation of the latter, it is always best to use the muffle furnace rather than a burner, since any unburnt hydrogen in the flame might attack the platinum, rendering it soft and spongy. It is essential, of course, to use a clean muffle and not one that has been used for scorifications or cupellations. The residue after ignition is now weighed, both alone and together with the crucible, and if desired the SiO_2 can now be determined direct by treating the insoluble matter with a few millilitres of HF and a drop of dilute H_2SO_4, evaporating to dryness, igniting, and weighing, the difference in the weight of the crucible and insoluble matter before and after treating with the HF being silica.

For accurate work, however, the insoluble matter after ignition should be fused in the crucible with about 5 gram of fusion mixture (roughly equal parts of Na_2CO_3 and K_2CO_3). When the mass is perfectly clear and free from unattacked particles the crucible is allowed to cool, being tilted somewhat to facilitate the easy removal of the melt. The melt is removed by squeezing the side of the crucible gently; and after placing the melt in a large evaporating dish, the crucible is rinsed with a few millilitres of dilute HCl, the washings being added to the dish, which is at once covered with a clock glass. A few more millilitres of HCl is added until no further effervescence occurs, the cover is rinsed and removed, and the dish is placed on the hot-plate and evaporated to dryness.

Considerable care must be taken to avoid spitting during the evaporation, any crystals appearing on the sides of the dish being gently pushed down into the liquid with a glass rod. When quite dry, the dish is baked strongly for an hour with the cover-glass on, removed from the plate, and cooled. When quite cold, a few millilitres of acid is added and then about 50 ml. hot water, and the solution is boiled to effect solution of the alkali salts. After settling, the insoluble matter, which should be pure silica, is collected on a close paper, washed thoroughly with boiling water, ignited, and weighed.

For great accuracy the silica is volatilised by heating in a platinum crucible with sulphuric and hydrofluoric acids, as described on page 115 in the general scheme for the analysis of silicates.

SULPHUR

Sulphur, in most ores with which the assayer has to deal, generally exists as the sulphide, but it is sometimes necessary to determine not only the total sulphur content, but also in which form it exists and in what proportion. A suitable procedure for either contingency is therefore given.

TOTAL SULPHUR

For copper or zinc concentrates take 0·3–0·5 gram and for roasted ores take 2 gram of the mineral and treat with about 15 ml. HNO_3 in a 250-ml. squat beaker. Allow to stand warm for a short time until the violent action is over, and then bring to the boil, keeping hot until the nitrous-oxide fumes are removed and the sulphur has melted into small beads. Add from a pipette a few drops of bromine (not Br water) directly on to the sulphur, warm to remove bromine, and if all the sulphur is not taken up repeat the additions of bromine. The reaction between the sulphur and the bromine is usually accompanied by a crackling noise, the absence of which is a good indication that all the sulphur has been taken up. Add a little HCl, rinse in and remove the cover, and evaporate carefully to dryness. When just dry, cool, add 5 ml. HCl, again evaporate dry. Bake for half an hour. A little potassium chlorate will aid in the removal of the HNO_3. Take up with a few ml. of HCl, warm to effect solution, and dilute to about 40 ml. with warm water. Make just ammoniacal, bring to the boil, allow to settle, and filter off the iron and insoluble matter together. Reprecipitate the iron if necessary. To the filtrate from the iron add HCl until just neutral; if copper is present, no indicator will be necessary, otherwise use methyl orange. Add about 3 or 4 ml. of HCl in excess, bring to the boil, add from a test tube 20 ml. of boiling barium-chloride solution (10-per-cent), continue to boil for about 10 minutes, and stand in a warm place to settle for at least 4 hours, preferably overnight. After settling the precipitate of barium sulphate can be collected on a fine paper (No. 32 or 42 Whatman), washed well with boiling water and with dilute (10-per-cent) HCl, ignited, and weighed. Factor: 0·1373.

An alternative method, which is rather more rapid and is very suitable for galenas and for all minerals low in silica, is as follows:

A suitable quantity of the mineral is weighed into a nickel crucible containing about 8–10 gram of sodium peroxide and the whole well mixed by stirring with a glass rod. Any particles adhering to the rod are brushed into the crucible with a camel-hair brush, and a little more peroxide is sprinkled over the charge. The crucible is now warmed cautiously, and when the contents are thoroughly molten it is gently rotated over the burner for about 3 minutes, being held in a pair of brass or bronze crucible tongs.

After cooling, the melt is extracted with warm water, the crucible removed and rinsed with HCl, the washings being added to the beaker. Further acid is carefully added to the solution until the precipitated iron is just dissolved, a slight excess being finally added, the solution boiled, and the sulphate precipitated with $BaCl_2$ as before.

SULPHUR AS SULPHIDE IN THE PRESENCE OF SULPHATES

Place a suitable quantity of the material in a conical flask to which has been fitted a thistle funnel and a delivery tube passing into an aqueous solution of cadmium acetate. Pour an excess of HCl down the funnel, warm to effect solution, finally boil to remove last traces of H_2S. Filter off precipitated cadmium sulphide and estimate either as $CdSO_4$ or volumetrically (see Cadmium).

SULPHUR AS SULPHATE IN THE PRESENCE OF SULPHIDES AND SULPHITES

The residue in the flask, after the removal of the H_2S, can be treated direct for sulphur, which can only exist as sulphate, since any sulphites present would have been destroyed by the HCl and the SO_2 driven over with the H_2S. When no sulphides exist, a suitable quantity of the material can be taken up direct in HCl, filtered, the acidity adjusted, and the barium chloride added to the boiling solution in the usual way. This is the standard method for the estimation of sulphur trioxide in zinc oxide.

SULPHUR AS SULPHITE IN THE PRESENCE OF SULPHIDES AND SULPHATES

If desired, the sulphur as SO_2 can be taken by difference from the total sulphur after the sulphides and sulphates have been determined. Where only sulphites and sulphates are present, a suitable portion of the material is dissolved in dilute (5-per-cent) H_2SO_4 in the cold, starch paste added, and the SO_2 titrated direct with decinormal or centinormal iodine solution. This method can also be adopted for sulphites and sulphides together, but where the latter are soluble under these conditions, the sulphides must be estimated separately and the sulphites taken by difference from the combined total.

A rapid method for the estimation of sulphur in the absence of iron, zinc and lead is as follows:

The solution containing the sulphur, which should be in the form of sulphate, is neutralized with ammonia and made just acid with HCl. It is brought to the boil and a solution of barium chromate in normal HCl is added in slight excess. The sulphates in solution are precipitated as barium sulphate, the equivalent chromic acid being released. After boiling for a minute or two, the excess barium chromate is precipitated by neutralizing the acid with $CaCO_3$ or ammonia—if the latter, the excess must be boiled off. The solution is now filtered, 5 ml. of HCl is added, and then, after cooling, KI is added and the chromic acid titrated with sodium-thiosulphate solution, using starch paste as indicator.

ALLOYS AND METALS

SHOULD the sample under examination be an alloy or metal, dissolve all that will dissolve in strong nitric acid, and then evaporate to a small bulk on the hot plate in the fume cupboard, add water, and if any residue remains after warming, this should be filtered and well washed with boiling water. The solution should then be examined by the general qualitative scheme for metals. The remaining residue is treated with a hot solution of tartaric acid, $H_2C_4H_4O_6$, and should a residue still remain, it should be filtered, and then examined for tin, and the filtrate for antimony.

PRINCIPAL METALLIC ORES AND MINERALS

Metal Type	*Name*	*Empirical Formula*	*Sp. Gr.*	*Hardness*
Silver	Argentite	Ag_2S	7·2–7·4	2—2·5
	Stephanite	$5Ag_2S.Sb_2S_3$	6·26	2–2·5
	Proustite	$3Ag_2S.As_2S_3$	5·4–5·6	2–2·5
	Horn Silver	$AgCl$	5·5	1–1·5
Lead	Galena	PbS	7·2–7·6	2·5–2·7
	Minium	Pb_3O_4	7·6	2–3
	Anglesite	$PbSO_4$	6·1–6·4	2·7–3
	Cerussite	$PbCO_3$	6·5	3–3·5
	Pyromorphite	$3Pb_3P_2O_8.PbCl_2$	6·5–7	3·5–4
	Crocoisite	$PbCrO_4$	5·9–6	2·5–3
	Wulfenite	$PbMoO_4$	6–7	2·7–3
	Cromfordite	$PbCl_2.PbCO_3$	6–6·3	2·7–3
Mercury	Cinnabar	HgS	9	2–2·5
Copper	Cuprite	Cu_2O	5·8–6·1	3·5–4
	Chalcopyrite	$CuFeS_2$	4·1–4·3	3·5–4
	Tenorite	CuO	6·2	3
	Copper Glance	Cu_2S	5·5–5·8	2·5–3
	Tetrahedrite	$4Cu_2S.Sb_2S_3$	4·5–5·1	3·5
	Malachite	$CuCO_3.Cu(OH)_2$	3·7–4	3·5–4
	Azurite	$2CuCO_3.Cu(OH)_2$	—	—
	Chrysocolla	$CuSiO_3.2H_2O$	2·2–2·3	2–4
Cadmium	Greenockite	CdS	4·8–4·9	3–3·5
Antimony	Stibnite	Sb_2S_3	4·5–4·6	2
Tin	Cassiterite	SnO_2	6·4–7·2	6–7
Iron	Magnetite	Fe_3O_4	4·9–6·3	5·5–6·5
	Hæmatite	Fe_2O_3	4·5–5·2	5·5–6·5
	Limonite	$2Fe_2O_3.3H_2O$	3·6–4	5–5·5
	Spathic Iron Ore	$FeCO_3$	3·7–3·9	3·5–4·5
	Iron Pyrites	FeS_2	4·8–5·1	6–6·5
	Mispickel	$FeAsS$	6·2–6·3	5·5–6
	Copperas	$FeSO_4.7H_2O$	1·8	2
	Vivianite	$Fe_3(PO_4)_2.8H_2O$	2·6	1·5–2

Metal Type	*Name*	*Empirical Formula*	*Sp. Gr.*	*Hardness*
Aluminium	Bauxite	$Al_2O_3.Fe_2O_3.H_2O$	—	—
	Cryolite	$6NaF.Al_2O_3$	2·9–3	2·5
	Corundum	Al_2O_3	3·9–4·1	9
	Spinel	$Al_2O_3.MgO$	3·5–3·6	8
	Alumstone	$K_2SO_4.3Al_2(SO_4)_3.6H_2O$	2·6–2·7	3·5–4
	Alunogene	$Al_2(SO_4)_3.18H_2O$	1·6–1·8	1·5–2·0
Chromium	Chromite	$FeO.MgO.Cr_2O_3$	4·3–4·5	5·5
Titanium	Rutile	TiO_2	4·2	6–6·5
	Ilmenite	$FeTiO_3$	4·5–5	5–6
	Titanite	$CaO.SiO_2.TiO_2$	3·4–3·6	5–5·5
Molybdenum	Molybdenite	MoS_2	4·4–4·8	1–1·5
	Molybdine	MoO_3	4·4–4·5	1–2
	Wolfram	$2FeWO_4.3MnWO_4$	7·1–7·8	5–5·5
Zinc	Blende	ZnS	3·9–4·2	3·5–4
	Calamine	$ZnCO_3$	4–4·5	5
	Zincite	ZnO	5·4–5·8	4–4·5
	Hemimorphite	$2ZnO.SiO_2.H_2O$	3·1–4	4·5–5
	Willemite	Zn_2SiO_4	4–4·1	5–5·5
Manganese	Pyrolusite	MnO_2	4·8–5	5·2–5·4
	Hausmannite	$MnO.Mn_2O_3$	4·7	5–5·5
	Rhodonite	$MnO.SiO_2$	3·4–3·6	5·5–5·6
Nickel	Kupfernickel	$NiAs$	7·3–7·4	5·5
	Chloanthite	$NiAs_2$	6·4–6·6	5·5–5·6
Cobalt	Smaltine	$CoAs_2$	6·4–7·2	5·5–6
	Erythine	$Co_3As_2O_3.8H_2O$	2·9–3	1·5–2·5
	Cobaltine	$CoAsS$	6·2	5·5
Uranium	Pitchblende	U_3O_4	6·4–6·8	5·5
	Calcium Uranite	$(CaO.3U_2O_3)P_2O_5$ $8H_2O$	3–3·2	2–2·5
Barium	Barytes	$BaSO_4$	4·3–4·7	2·5–3·5
	Witherite	$BaCO_3$	4·3–4·35	3–3·7
	Barytocalcite	$BaCO_3.CaCO_3$	3·6	4
Strontium	Celestine	$SrSO_4$	3·9	3–3·5
	Strontianite	$SrCO_3$	3·6–3·7	3
Calcium	Calcite	$CaCO_3$	2·6–2·7	2·5–3·5
	Dolomite	$CaCO_3.MgCO_3$	2·8–2·9	3·5–4
	Gypsum	$CaSO_4.2H_2O$	2·3	1·5–2
	Anhydrite	$CaSO_4$	2·8–2·9	3–3·5
	Apatite	$3Ca_3P_2O_8.CaCl_2$	2·9–3·3	4·5–5
	Fluorspar	CaF_2	3–3·25	4
Magnesium	Magnesite	$MgCO_3$	2·8–3	3·5–4·5
	Brucite	$Mg(OH)_2$	2·3	2·5

Potassium and sodium—see Stassfurt deposits (page 87).

PART III

TYPICAL ANALYSES OF ORES

ASSAY OF SILVER AND GOLD ORES

THESE two metals are usually found associated and can be estimated conveniently only by dry assay. Three separate operations are usually necessary: first, the pot assay, in which the precious metals are obtained in a button of lead; secondly, the reduction of the button by scorification; and lastly the removal of the lead by cupellation. It is the general practice to report gold and silver not as percentages, but as ounces troy per ton avoirdupois, so that it will be found convenient to use " assay ton "[*] weights in their assay. These weights are calculated so that where one assay ton is taken for an assay, one milligram in the resultant bead is equivalent to one ounce (Troy) per ton of bullion.

POT ASSAY

The following charge is made up:

Ore	1·0 to 2 A.T.
Litharge	75 gram
Flour	3–4 gram
Soda ash	60 gram
Borax	35 gram

A little of the borax is retained as a cover and the rest of the charge, after well mixing, is transferred to a suitable crucible. The rest of the borax is added, and then one or two pieces of hoop iron (iron nails will serve) are inserted. The crucible is placed in a wind furnace at a dull red heat for about a quarter of an hour, after which the temperature is gradually raised until the whole charge is fused and the reaction is over. The pieces of iron are removed and the charge poured into a mould. When cold the slag is removed from the button, which is cleaned by hammering, followed by brushing with a nail brush.

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[*] Since 1 ton contains 32,667 ozs. (Troy), the weight taken for the assay (one assay ton) is 32·7 gram.

SCORIFICATION *

The button obtained from the pot assay is weighed, and if it is over, say, 50 gram or is hard or brittle (showing the presence of Sb, Sn or Cu), it should be scorified. The button is placed in a scorifier† together with about a gram of borax in a very hot muffle furnace. After a time a portion of the lead oxidizes and unites with the borax to form a fluid slag, which dissolves the impurities. The slag gradually covers the button, which appears as an " eye " in the centre of the dish, steadily diminishing in size. When finally covered, about 0·1 gram of powdered anthracite is added, and the muffle door partially closed until all action has ceased. The scorifier is now removed from the muffle and the contents immediately poured into the mould. When quite cold the button is detached from the slag and cleaned in the usual way. It is essential that the muffle is very hot for this assay, and the door should be kept closed until the whole is fluid, after which the top of the muffle door can be removed to allow oxidation to take place.

CUPELLATION ‡

The button from the scorification is placed in a red-hot cupel§ in a muffle, the door of which must be kept closed until cupellation commences, when the door is partially opened to supply the necessary air. The cupel should be allowed to remain in the muffle for about 3 minutes after cupellation ceases, after which it is allowed to cool gradually (it is safest to place another cupel over the trial before removing from the muffle, to avoid loss by spitting). The bead is cleaned by squeezing and brushing, and is weighed on the assay balance.

PARTING ||

This process is carried out to obtain the relative percentages of silver and gold in the product from cupellation. It is necessary to have present at least two and a half times as much silver as gold in the bead, so that if the proportion of silver is deficient, more must be added by means of a second cupellation. The bead is hammered flat and then dropped into a test tube containing hot dilute HNO_3 (specific gravity 1·2). The contents are boiled and then washed by decantation with distilled water, and the residual gold is finally transferred to an anneal-

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[*] Oxidation of lead and slagging of impurities.

[†] A scorifier is a shallow fireclay dish.

[‡] Recovery of silver and gold.

[§] A cupel is a shallow cup made of bone-ash or some other absorbent material, which absorbs substances that wet the surface whilst hot.

[||] Separation of silver from gold.

ing cup and heated to redness over a bunsen. The gold so obtained is brushed on to the pan of the assay balance and weighed, the silver being taken by difference from the weight of the bead after the first cupellation.

ESTIMATION OF ZINC IN BURMA ZINC CONCENTRATES

Weigh out 1 gram of the finely crushed ore in a 250-ml. squat beaker and dissolve in aqua regia. Fume with 25 ml. 50-per-cent H_2SO_4, and allow to cool. Digest with 50 ml. of water until solution is complete, cool, and pass H_2S. When saturated, add 50 ml. of distilled water, saturated with H_2S.

Filter and wash with $2\frac{1}{2}$-per-cent solution of H_2SO_4 containing H_2S, and discard precipitate.

Filtrate. Boil off H_2S, cool quickly and add ammonia from a beaker until nearly neutral, using methyl orange as indicator. Now thoroughly cool, exactly neutralize, and add about 5 or 6 drops of normal H_2SO_4. Pass H_2S, dilute to 600 ml. with H_2S water, and pass H_2S for at least 2 hours whilst warm.

Allow to settle, and filter through a double 40 or 30 Whatman paper, 12·5 cm., washing once with $2\frac{1}{2}$-per-cent solution of H_2SO_4 containing H_2S as before. Wash back precipitate with hot water into original beaker, cleaning paper with about 10 ml. of strong HCl.

Boil off H_2S, add 2 or 3 drops of HNO_3, make just neutral, and add 3 ml. excess HCl.

Titrate whilst boiling with potassium-ferrocyanide solution, using drops of uranium nitrate or acetate as outside indicator on a white porcelain tile or spot plate.

DETERMINATION OF METALLIC ZINC IN ZINC DUST

Many methods have been proposed for the accurate estimation of metallic zinc in this material, one of the uses of which is the precipitation of gold from its cyanide solution. It is as well to point out that where the dust is to be used for this purpose its metallic content is not the sole criterion of its value, since a sample of dust assaying, say, 95 per cent metallic zinc and passing a 500-mesh sieve might quite reasonably be more efficient than another assaying 99 per cent, but being fine enough to pass only a 200-mesh sieve. For this reason a method is also given to determine the “ efficiency ” of a dust.

For the determination of the metallic content only, a selection of two methods is given, both of which were devised by one of us, and have given excellent results.

Method 1. A standard solution of $CuSO_4$ is prepared by dissolving 100 gram of the pure (acid-free) crystals in water, and making the solution up to 5 litre. (1 ml. will contain approximately 5 mg. Cu.) 100 ml. of this solution is pipetted out into a 500-ml. conical flask, a few drops of soda-ash solution is added and then a slight excess of acetic acid, 3 gram of potassium iodide is added and the solution is titrated with standard thiosulphate solution (40 gram per litre).

(Most assayers object to the use of soda ash on the grounds that sodium acetate tends to give low results with a copper assay. For general purposes the authors always use ammonia, but find it impossible to obtain the same perfect end-point in this assay when using ammonia as is obtained with soda-ash solution—of which, of course, only a very small quantity is used.)

400 ml. of the standard thiosulphate solution is now withdrawn from the bulk (solution A) and diluted to 1 litre (solution B). 1 gram of the sample is accurately weighed into a 450-ml. conical flask, and is treated with 250 ml. of the copper solution, added by means of a 250-ml. pipette, if such is available. Any lumps formed are rubbed out against the sides and bottom of the beaker by means of a dry policeman, and after occasional stirring the solution is allowed to settle for half an hour. The solution is now filtered through a *close* paper (No. 41 or 31 Whatman preferably), and when sufficient has been obtained, 100 ml. is transferred by means of a pipette into a clean 500-ml. conical flask, and is titrated with solution B. The percentage of metallic zinc is now obtained by the following calculations:

1 ml. solution A$=t$ gram of copper.
250 ml. $CuSO_4=x$ ml. of solution A ($=xt$ gram Cu).
100 ml. filtrate$=y$ ml. solution B.
Percentage metallic zinc: $t(x-y)\times 1{\cdot}028\times 100$.

Method 2. The total zinc content is first determined by treating 0·5 to 1 gram of the sample with ammonium chloride and HCl, and titrating the solution with potassium-ferrocyanide solution in the usual way. 5 gram of the dust is now weighed into a 450-ml. conical flask and shaken for 5 minutes with 50 ml. of " Tambon "* solution. The solution is now rapidly filtered through a close paper, washed with hot water, and, after adjusting the acidity to 3 ml. excess HCl, the filtrate is titrated with potassium-ferrocyanide solution. The difference between the total zinc per cent and the soluble zinc per cent is the metallic zinc.

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* See page 123.

Efficiency. This is defined as the amount of gold which can be precipitated from cyanide solution by the addition of a standard weight of Zn. For laboratory purposes silver is usually substituted for gold, and since in this reaction zinc is monovalent, $K.Ag(CN)_2 + Zn = K.Zn(CN)_2 + Ag$, 100 per cent efficiency would be obtained by the precipitation of 1·08 gram of Ag by the use of 0·6537 gram Zn.

0·1 gram of the dust is weighed into a stoppered bottle and treated with an excess of a solution of AgCN in KCN. The bottle is agitated for an hour, after which the solution is decanted through a filter paper, the precipitate washed on and then washed free from cyanide with hot water. The paper and precipitate are ignited in a porcelain crucible and the residue brushed into a small square of Ag-free lead foil, which is now rolled up and cupelled. Where 0·1 gram of dust is taken for the trial, the weight of the button of silver multiplied by 100 and divided by 0·1652 is the percentage efficiency. Silver solution: 13·4 gram AgCN is dissolved in a little KCN, and the solution diluted to a litre. 100 ml. is taken for a determination.

ESTIMATION OF LEAD AS MOLYBDATE

This method has no particular value as compared with the thiosulphate estimation previously described, except that it can be used as a very good check on results obtained by other methods which might have been questioned, or for referee assays where assays are to be undertaken by at least two methods.

A quantity of material containing not more than 0·100 gram is dissolved in HCl or aqua regia and evaporated to a low bulk on the hot plate. When nearly dry, from 10 to 40 ml. (according to the amount of sample used) strong H_2SO_4 is added, the whole well stirred and then evaporation continued until strong fumes of sulphur trioxide are evolved. The beaker is allowed to cool and the mass taken up with a few millilitres of cold water, well stirred, and then boiling water is added until the beaker is about one-third full. The solution is boiled for about 10 minutes and then allowed to stand aside for at least 4 hours to settle. The lead sulphate is collected on a wad of paper pulp, washed with normal H_2SO_4, and returned to the beaker. About 5 gram of solid ammonium acetate is added and about 30 to 40 ml hot water. The solution is boiled for about 15 minutes and again passed through pulp. The filtrate is returned to the original beaker, brought to the boil, and about 20 ml. of 1-per-cent ammonium molybdate solution is added. The solution is allowed to boil for a further 10 minutes and then allowed to settle. The precipitate is collected on a fine paper, washed thoroughly with hot water, and the paper and precipitate transferred to a porcelain crucible or small roasting dish, ignited in the muffle, and weighed.

ESTIMATION OF FERROUS IRON IN IRON ORE

Two or more gram of the material is weighed into a 500-ml. flat-bottomed flask, to which is added a few small pieces of pure chalk. Sufficient water is added to cover the bottom of the flask and then a few millilitres of strong H_2SO_4 is added. The flask is warmed to effect solution, which is diluted to about 250 ml. with water and titrated to a permanent pink colour with standard potassium-permanganate solution.

DETERMINATION OF MANGANESE DIOXIDE IN MANGANESE ORES

0·5 gram of the finely crushed ore is placed in a conical flask and treated with 50 ml. of standard ferrous-sulphate solution and 10 ml. strong HCl. The flask is gently warmed to effect solution, cooled somewhat, and then diluted to about 300 ml. with cold distilled water. The excess ferrous iron is now immediately titrated with standard potassium-dichromate solution.

An alternative method depends on the estimation of the available chlorine produced by the action of HCl on the crushed mineral.

0·5 gram of the material is placed in a distillation flask, in the neck of which is placed a thistle funnel. The side tube is connected to a length of glass tubing leading into a flask half full of water containing 3 gram of potassium iodide. The latter flask is itself placed in a bowl of cold water or a cooling tank. A sufficient quantity of water is poured down the funnel to cover the bottom of the flask, and then a quantity of strong HCl. Heat is applied, at first gently and then more strongly, until solution is complete. A few millilitres of dilute salt solution is then poured down the funnel so as to drive over the last traces of chlorine, and the apparatus is disconnected before the flame is removed. Starch solution is added to the distillate and the freed iodine immediately titrated with standard sodium-thiosulphate solution.

COLORIMETRIC ESTIMATION OF LEAD IN ZINC OXIDE

This method is exceptionally useful for giving a rough guide as to the nature of an oxide, and will enable the operator to decide the best procedure to adopt in carrying out the subsequent complete assay.

A series of standard samples are required containing from, say, 20 to 200 parts per million of lead, in which the exact figure has been determined by the thiosulphate-chromate method. Where the origin of the sample is unknown it is of advantage to test (first) a small portion by spotting with yellow ammonium sulphide, which will give some indication as to the probable quality. The procedure for the test is as follows:

2 gram of the sample is dissolved in the minimum quantity of HCl in a small beaker, warmed if necessary, and diluted with cold water to a bulk of between 30 and 35 ml. The solution, filtered if necessary, is made strongly alkaline with ammonia and then transferred to a Nessler tube standing on a white porcelain plate. Two drops of strong sodium-sulphide solution are now added, and the density of the colour is at once compared with several standard samples treated in exactly the same manner.

GENERAL SCHEME FOR THE COMPLETE ASSAY OF A ZINC ORE

Weigh out 5 gram of the dried ore and dissolve in aqua regia. Filter on tared papers, dry, and weigh the insoluble matter; ignite and weigh again. The difference in weight is carbonaceous matter. Treat the insoluble matter with HF to determine silica, dissolve the residue in HCl and add to the main bulk.

Filtrate. Evaporate slowly on the hot plate until almost dry, add 20 ml. strong H_2SO_4, and continue to evaporate until copious fumes of SO_3 are evolved. Cool, add sufficient cold water to soften the melt and then hot water to a bulk of about 300 ml. Boil for about 10 minutes and allow to settle, preferably overnight. Filter through paper pulp and estimate lead as chromate by thiosulphate. Make up the filtrate to 500 ml. and pipette out 100 ml., out of which estimate the iron, alumina and zinc. Pass H_2S through the balance of the trial, filter through pulp, treating precipitate first with NaHS, then with H_2SO_4 (20-per-cent), and lastly dilute HNO_3 and bromine water. Estimate antimony, arsenic, and tin (if any), in the first extract, cadmium in the second and copper in the last. The copper extract is preferably taken low with sulphuric acid, and, while fuming, treated with drops of HNO_3 from a dropping bottle to remove any traces of carbonaceous matter from the paper pulp.

The filtrate from the Group II separation can be utilized to estimate the lime and magnesia, the latter being determined after removal of the zinc by gassing in very slightly acid condition. Nickel and cobalt can also be estimated from the filtrate from the magnesia by the addition of ammonium sulphide, or preferably by gassing in alkaline solution. Sulphur, chlorine and the alkalies (if any) are estimated separately.

GENERAL SCHEME FOR THE COMPLETE ASSAY OF A MANGANESE ORE

Weigh out 5 gram of the dried ore into a 600-ml. squat beaker and after thoroughly wetting with HNO_3, add sufficient HCl to effect solution. When solution is complete, rinse in the cover and evaporate slowly to dryness. Bake for 15 minutes, replace dry cover, and continue to bake for about a further half an hour. Allow to cool, moisten with a little HCl (between 5 and 10 ml.), and take up with hot water. Boil until dissolved and filter through a close paper, washing well with hot water and dilute HCl. Ignite insolubles, weigh and estimate silica with HF. Treat residue from silica estimation with HCl and filter, collecting filtrate in the main bulk.

Transfer main bulk to a 500-ml. measuring flask and make up to the mark with cold water. Well mix and pipette out 25 ml. for Mn by basic acetate method. (Volhard's method can be used, provided the standard solution has been checked by an ore of similar grade.) Pipette out also the following charges:

100 ml. for Fe, Al, Ca, Mg.
100 ml. for phosphorus.
200 ml. for Cu, Pb, and Zn.

Weigh out separate 2-gram charges and estimate sulphur and chlorine, and a further 0·5 gram for MnO_2.* Although FeO is possibly present, it would be at once oxidized by the addition of HCl to the ore, the MnO_2 being reduced by the same amount. ($MnO_2+2FeO = MnO+Fe_2O_3$.) Mn as dioxide deducted from total Mn is the Mn as monoxide. Cu is estimated conveniently by passing H_2S after fuming and removing lead (which is estimated as chromate by thiosulphate method), the precipitate being taken up with HNO_3 and bromine water, evaporated nearly to dryness and the Cu estimated by colour. The ore may also contain barium sulphate, which can be estimated by fusing a portion with fusion mixture in a platinum crucible, extracting the melt with dilute HCl, baking to remove silica, and filtering, keeping the bulk as low as possible. The filtrate is taken to fuming with H_2SO_4, the lead and barium filtered off together, washed back and boiled with ammonium acetate and refiltered, ignited, and weighed as $BaSO_4$.

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* Determined as shown on page 104.

Alkalies are estimated by fusing direct with ammonium chloride and chalk, as on page 117

PART IV

NON-METALLIC MINERALS

SILICA AND THE SILICATES

Silica. Silica is found in nature in several crystalline forms, for example, as in quartz and tridymite, and as amorphous silica. In free and combined forms silica is said to represent nearly 66 per cent of the earth's crust. Naturally occurring silicas may be classified as follows:

1. Varieties of quartz, including rock crystal, quartzite, quartz sand, sandstone, sand and various coloured forms that can be used as semi-precious stones.
2. Varieties of chalcedony, including carnelian, agate, onyx and flint.
3. Varieties of jasper, including ribbon jasper, hornstone and chert.
4. Varieties of opal, or hydrated silica.
5. Tridymite and related minerals.
6. Diatomaceous earths and amorphous silicas.

1. *Varieties of Quartz. Quartz* crystallizes in the hexagonal system, nearly always in hexagonal prisms terminated by hexagonal pyramids. The colourless pure forms are known as rock crystal; the " pebble " of the opticians. Hardness 7; specific gravity 2·65. Sometimes the crystals contain cavities party filled with water or with liquid carbon dioxide. There are also found varieties containing inclusions of other minerals, such as rutile, chlorite or asbestos, which have been enclosed by the quartz.

Quartzite is nearly pure silica, as is *Quartz-sand.* Sandstone is silica associated with iron oxide and clay in varying proportions.

Aventurine is a type of quartz that contains scales of mica. There is also ferruginous quartz, sometimes red and at other times of a brown colour, due to Fe_2O_3.

Cats-eye is quartz with a minutely fibrous structure, sometimes due to asbestos giving it a silky lustre on polished surfaces when cut " en cabochon." *Amethyst* is a violet-coloured variety of quartz.

2. *Varieties of Chalcedony. Chalcedony* is not crystallized, but has a crypto-crystalline structure, being essentially a mixture of quartz and

amorphous silica. *Agate* is a mixture of crystalline and amorphous silica in concentric layers, forming masses which often contain hollows in the centre in which crystals of quartz or amethyst are developed. *Onyx* and *Sardonyx* are banded varieties of chalcedony. *Flint* is a grey or black variety. Specific gravity, 2·6; hardness 6·5.

Some varieties of chalcedony are characteristically coloured as follows:

Carnelian is red, *Sard* is red-brown, *Plasma* is olive green, *Chrysoprase* is apple green.

3. *Varieties of Jasper*. *Jasper* is a compact, opaque variety of silica coloured with hæmatite, Fe_2O_3, or limonite, $2Fe_2O_3.3H_2O$, either red, brown, or yellow.

Banded Jasper, also known as *Ribbon Jasper*, also exists in various shades of colour. *Bloodstone* is green jasper with red spots, while *Chert* and *Hornstone* are impure varieties.

4. *Opal* is a hydrated amorphous silica, the amount of water varying from 3 to 12 per cent. Hungary, Honduras and Queensland, in Australia, have in the past produced the finest specimens; with a fine play of colours due to internal reflections. Specific gravity 1·9–2·2; hardness 6.

5. *Tridymite* crystallizes in the triclinic system. Hardness 7; specific gravity 2·3. Tridymite is often found in trachyte from the Andes and Japan. It is soluble in a boiling solution of sodium carbonate.

6. Amorphous silica. A fine amorphous silica from the Greek archipelago gave the following analysis:

Silica	97·85	per cent
Titanic oxide	0·12	,,
Alumina	0·34	,,
Ferric oxide	0·02	,,
Manganese oxide	Nil	
Calcium oxide	0·07	,,
Alkalies	0·64	,,
Combined water	0·71	,,
	100·00	,,

SILICATE MINERALS

Silicate minerals may be divided conveniently into the following main groups:

(1) Aluminosilicates
(2) Aluminofluosilicates
(3) Magnesium silicates.

Alternatively they may be divided into the two groups:

(a) Igneous and igneous metamorphic rocks;
(b) Sedimentary and sedimentary metamorphic rocks.

1. *ALUMINOSILICATES.*

Felspars. The felspars are very important varieties of mineral silicates containing potash, soda, or lime. The potash felspars crystallize in the monoclinic system, except microcline, while the soda and lime felspars crystallize in the triclinic system. The lime felspars are more easily decomposed by acids than the potash and soda varieties. They enter very largely into the composition of igneous rocks.

The following are the more important monoclinic felspars:

Orthoclase is ordinary potash felspar with very perfect cleavage planes parallel to the base and clinodiagonal, forming a right angle. Hardness 6; specific gravity 2·55. *Adularia* is a colourless and sub-transparent variety and includes moonstone or sunstone. *Sanidine* is a glassy felspar, being a vitreous variety, and occurs in volcanic rocks. *Amazonstone* has a green colour due to copper salts.

The triclinic felspars include the following:

Albite, a soda felspar found in granite and other crystalline rocks. Hardness 6–7; specific gravity 2·6–2·65. *Anorthite*, a lime felspar found in many old lavas, and in the diorite of Corsica. Hardness 6–7; specific gravity 2·75. *Labradorite*, a lime-soda felspar, common in basalt and dolerite. It often shows a beautiful iridescent play of colours. Hardness 6; specific gravity 2·7. *Oligoclase*, a soda-lime felspar; a constituent of many igneous rocks. Hardness 6; specific gravity 2·65. *Andesine*, a soda and lime felspar found in the trachyte of the Andes and other localities. Hardness 6; specific gravity 2·7. Frequently found twinned like albite. *Microcline* is a tricalcium potash felspar with a characteristic crosshatching. *Nepheline* is an essential constituent of phonolite and occurs in many lavas. Closely resembling felspar in composition. Hardness 5–6; specific gravity 2·6. *Leucite*, colour white or grey, is a constituent of recent volcanic rocks. Hardness 5·5–6; specific gravity 2·4–2·6.

CLAYS

Argillaceous sedimentary rocks, mainly clays, shales and slates, are impure hydrated aluminium silicates. Those possessing valuable and characteristic properties include:

Fullers' Earth. This is a mixture of magnesium-aluminium silicates, produced by the weathering of igneous rocks. The silicates are present as the minerals *Attapulgite* and *Montmorillonite*, which are found in

Georgia and Florida and are commonly used as absorbents in oil and sugar refining. Typical compositions are SiO_2, 45–70 per cent; Al_2O_3, 10–20 per cent; MgO, 3–12 per cent; Fe_2O_3, 3–5 per cent. The clay from Attapulgus, from which the mineral derives its name, has the empirical formula $Mg_5Si_8O_{20}.10H_2O$. Empirical formula for a typical montmorillonite is $Al_5Mg.Na.Si_{12}O_{30}.3H_2O$. The montmorillonite minerals are the principal constituents of the important *Bentonite* clays, used in foundry sands and as protective colloids.

Sepiolite (or *Meerschaum*), is a fibrous hydrated magnesium silicate whose properties are similar to those of Attapulgite. Formula $2MgO.3SiO_2.2H_2O$.

Kieselguhr, and the related diatomaceous earths, are forms of hydrated silica derived from the silicious skeletons of diatoms associated with varying proportions of impurities. Typical analyses are SiO_2, 65–88 per cent; Al_2O_3, 2–12 per cent; Fe_2O_3, traces to 3 per cent; magnesium, calcium, alkalies, traces; water 5 to 14 per cent. Largely used as absorbent earths and filter aids.

Tripoli Powder, is a silicious earth resulting from the weathering and degradation of chert. When pure, it is nearly white, and is used as a polishing and abrasive powder.

Kaolin or *China Clay*, $Al_2O_3.2SiO_2.2H_2O$, is formed from felspar by the removal of alkaline silicates and by hydration. The following are a number of British china clays analysed by the authors:

Sample	Silica (SiO_2)	Alumina (Al_2O_3)	Ferric Oxide (Fe_2O_3)	Lime (CaO)	Magnesia (MgO)	Total Water	Alkalies (K_2O)	Total
1 ..	46·21	39·82	0·38	0·45	0·10	12·81	0·23	100·00
2 ..	46·32	39·76	0·40	0·41	0·11	12·69	0·31	100·00
3 ..	47·60	38·26	0·55	0·42	0·20	12·40	0·57	100·00
4 ..	47·74	37·66	0·58	0·61	0·22	12·60	0·59	100·00
5 ..	45·74	36·84	1·86	0·60	0·11	11·06	3·79	100·00
6 ..	46·46	37·40	2·00	0·86	0·21	11·81	1·26	100·00
7 ..	48·16	38·45	2·06	0·50	0·14	10·59	0·10	100·00
8 ..	46·20	36·23	1·57	0·76	0·11	11·00	4·13	100·00
9 ..	46·60	37·48	1·26	0·64	0·22	12·74	1·06	100·00
10 ..	46·28	38·38	1·03	0·72	0·15	12·78	0·66	100·00
11 ..	46·38	39·00	0·79	0·58	0·11	12·70	0·44	100·00
12 ..	47·26	37·84	1·08	0·54	0·29	12·07	0·82	100·00

Idocrase is a silicate of lime and alumina: crystalline structure tetragonal, the common form being modified tetragonal prisms. Hardness 6·5; specific gravity 3·34–3·45.

Zeolites. These are double hydrated silicates of aluminium and calcium or sodium yielding gelatinous silicates with acids, and occur in amygdaloid rocks and in basalt, often found in cavities. Zeolites include such minerals as *Natroline*, *Analcine*, *Chabasite*, *Prehnite*, *Thomsonite*, *Stilbite*, *Henlandite* and several others. They possess the property of exchanging bases with salts in solution in water, that is Na for Ca and vice versa. Hence their use in base exchange water softeners.

MICACEOUS MINERALS

The micas are a group of complex silicates of aluminium with varying proportions of the alkalies, magnesium, iron (ferric and ferrous), hydrogen, fluorine and water. The principal members of the group are *Muscovite*, *Biotite*, *Phlogopite* and *Lepidolite*. They are characterized by the readiness with which they split into plates or sheets possessing varying degrees of flexibility and toughness. All crystallize in the monoclinic system.

Muscovite or *Common Mica*, $3Al_2O_3.K_2O.6SiO_2.2H_2O$: Hardness 2; specific gravity 2·7. Chief supplies from India, Canada and the U.S.A.

Biotite $(H.KMg.Fe)_2.Al.Fe_2(SiO_4)_3.H_2O$. Hardness 2–2·5; specific gravity 2·7–3·1.

Vermiculite is a metamorphosed form of the mineral biotite, of red-brown, micaceous appearance. Possesses the property of exfoliation on heating, due to the generation of steam within the layers, producng a product some 30 times the volume of the orignal mineral and with apparent density 4–10 lb./ft.^{3}.

Phlogopite $(HKMgF)_3.Mg_3Al(SiO_4)_3.H_2O$. Found in the crystalline limestones of North America. Hardness 2–3. Specific gravity 2·7–3·1.

Lepidolite. $KLi.(Al.OH.F)_2.Al(SiO_3)_3.H_2O$.

COMPLEX ALUMINIUM SILICATES

Chlorite is a silicate of alumina, magnesia and ferrous oxide, with an olive-green colour. $6MgO.Al_2O_3.3SO_2.4H_2O$.

Tourmaline is a mineral of complicated constitution containing boric acid, H_3BO_3, as an essential constituent, and, frequently, phosphoric acid and fluorine.

The *Garnets* are silicates of protoxides and sesquioxides, $3RO.R_2O_33SiO_2$, the protoxides being lime and magnesia and the sesquioxides iron and manganese. They all crystallize in the cubic system, sometimes as rhombic dodecahedra. Hardness 6·5–7·5; specific gravity 3·4–4·3.

Beryl or *Aquamarine*, when a deep green colour is known as an emerald, and contains the element glucinum or beryllium. Hardness 7·5; specific gravity 2·7.

Topaz is an aluminium silicate with part of the oxygen replaced by fluorine. Hardness 8; specific gravity 3·4–3·65.

Zircon is a silicate of zirconium: widely distributed in rocks as minute grains. Hardness 7·5; specific gravity 4·4–4·7.

ASBESTIFORM MINERALS

These include the serpentine and hornblende varieties of asbestos used in commerce, namely *Chrysotile*, *Tremolite*, *Crocidolite* and *Amosite*. The serpentine minerals have the composition $3MgO.2SiO_2.2H_2O$, whilst the hornblende group are variations on the composition $Ca(MgFe)_3.4SiO_2$.

Chrysotile, $3MgO.2SiO_2.2H_2O$, the white flexible asbestos used for spinning textiles, occurs in narrow veins traversing serpentine rocks.

Tremolite, $CaO.3MgO.4SiO_2$, is a calcium-magnesium silicate, that occurs as rather long but brittle fibres.

Crocidolite, $NaFe(SiO_3)_2.FeSiO_3.H_2O$, the "blue" asbestos of commerce, is a soda-iron-magnesium silicate. The fibres are coarser than those of chrysotile, but can be spun into textiles.

Actinolite, is a green-coloured fibrous mineral. It is a calcium-iron-magnesium silicate and, with tremolite, crocidolite and amosite, forms the hornblende group of asbestiform minerals.

Amosite is a calcium-magnesium silicate, consisting of long, fine, but non-flexible fibres, used for this reason for insulating compositions.

Anthophyllite is a magnesium-iron silicate of apparent fibrous structure. The fibres are, however, exceeding weak and fall to powder on handling. For this reason the mineral is not of much industrial importance.

Massive *Serpentine* is found in Cornwall, Canada and Rhodesia. It is coloured shades of green; specific gravity 2·5–2·7; hardness 3–4.

Hornblende is a white or greyish mineral, often showing pseudo-fibrous structure; specific gravity 3–3·5; hardness 5–6. $FeO.3MgO.4SiO_2$.

Other commonly occurring magnesium silicates of importance are *Talc*, $3MgO.SiO_2.H_2O$ and *Steatite*, $3MgO.4SiO_2$.

The following is a list of the more important silicate minerals:

Orthoclase, $K_2O.Al_2O_3.6SiO_2$
Albite, $Na_2O.Al_2O_3.6SiO_2$
Oligoclase, $3Na_2O.CaO.4Al_2O_3.20SiO_2$
Andesite, $Na_2O.CaO.2Al_2O_3.8SiO_2$
Labradorite, $Na_2O.3CaO.4Al_2O_3.12SiO_2$
Anorthite, $CaO.Al_2O_3.2SiO_2$

Nepheline, $(NaK)_2.Al_2O_3.2SiO_2$
Leucite, $K_2O.Al_2O_3.4SiO_2$
Hornblende, $FeO.3MgO.4SiO_2$
Augite, $CaO.MgO.2SiO_2$
Tremolite, $CaO.3MgO.4SiO_2$
Diallage, $CaO.FeO.MgO.3SiO_2$
Olivine, $MgO.FeO.SiO_2$
Muscovite, $K_2O.3Al_2O_3.6SiO_2$
Biotite, $3MgO.Al_2O_3.3SiO_2$
Andalusite, $Al_2O_3.SiO_2$
Talc, $3MgO.SiO_2.H_2O$
Steatite, $3MgO.4SiO_2$
Meerschaum, $2MgO.3SiO_2.2H_2O$
Chlorite, $6MgO.Al_2O_3.3SiO_2.4H_2O$
Serpentine, $3MgO.2SiO_2.2H_2O$
Epidote, $4CaO.H_2O.3(Al.Fe)_2.6SiO_2$
Pyrope, $3MgO.Al_2O_3.3SiO_2$
Almandine, $3FeO.Al_2O_3.3SiO_2$
Beryl, $3BeO.Al_2O_3.6SiO_2$
Zircon, $ZrO_2.SiO_2$
Topaz, $5(Al_2O_3.SiO_2)Al_2SiF_{10}$
Prehnite, $2CaO.2Al_2O_3.3SiO_2.2H_2O$
Stilbite, $CaO.Al_2O_3.6SiO_2.6H_2O$
Kaolin, $Al_2O_3.2SiO_2.2H_2O$
Natrolite, $Na_2O.Al_2O_3.3SiO_2.2H_2O$
Muscovite, $3Al_2O_3.K_2O.6SiO_2.2H_2O$
Chrysotile, $3MgO.2SiO_2.2H_2O$
Crocidolite, $NaFe(SiO_3)_2.FeSiO_3.H_2O$
Kaolin, $Al_2O_3.2SiO_2.2H_2O$

GENERAL SCHEME FOR THE ANALYSIS OF SILICATE MINERALS

Take 1 gram of the finely ground sample and mix intimately on a sheet of glazed paper with 10 gram of pure anhydrous sodium carbonate. Transfer to a platinum basin and fuse for approximately 40 minutes, or until fusion is complete, at a temperature between 1100° C. and 1200° C. Cool and detach the melt from the crucible, allowing it to fall into an evaporating dish containing distilled water. Wash the crucible with water, then dilute hydrochloric acid followed by water and pour into the dish containing the melt. The bulk of the solution should be about 200 ml.

Silica. Add carefully an excess of hydrochloric acid. Evaporate to dryness and bake for 1 hour at 120° C. Cool, moisten with concentrated hydrochloric acid, evaporate to dryness and bake for $\frac{1}{2}$ hour at 120° C. Cool, moisten with concentrated hydrochloric acid, take up in water and leave for 10 minutes. Filter and wash with hot 1 : 1 hydrochloric acid, then with cold water, hot dilute hydrochloric acid and cold water in turn, followed by hot water. Ignite in a tared platinum crucible and reserve the residue.

Evaporate the filtrate and washings to dryness and bake as before. Moisten with concentrated hydrochloric acid, evaporate and bake again. Take up with 1 : 1 hydrochloric acid and wash well. Filter and add the filter paper to the platinum crucible. Ignite, cool and weigh. The increase in weight gives the crude silica.

Place the crucible and contents in a fume cupboard; moisten with a few drops of concentrated sulphuric acid; then add water to give a thin paste. Add hydrochloric acid till the crucible is approximately two-thirds full and evaporate cautiously at gentle heat. Slowly raise to full heat until all volatile matter disappears.

$$\text{Loss of weight} = SiO_2$$

If any residue remains in the crucible, fuse with potassium bisulphate. Cool, digest with water, and add to the main filtrate.

Alumina, Ferric Oxide and *Titania.* Add 20 ml. of a saturated solution of ammonium chloride to the combined filtrates and boil. Remove from the hot plate and add, with constant stirring, 1 : 1 ammonium hydroxide in slight excess. Cover with a clock glass and bring to the boil. Remove and filter immediately, washing with hot water and reserving the filtrate. Transfer the precipitate from the filter paper to a beaker; redissolve in 30 ml. of hydrochloric acid and make up to 250 ml. with distilled water. Cover and boil. Remove from the hot plate and add 1 : 1 ammonium hydroxide in slight excess. Boil, filter through a No. 31 Whatman filter paper and wash with hot water. Add this filtrate to the previous one. Dry, ignite, cool and weigh as mixed oxides.

Mix the above residue with 5 gram of potassium bisulphate and heat in a muffle to red heat for $\frac{1}{2}$ hour. Allow to cool and transfer to a beaker, using hot distilled water. Cover and boil for 15 minutes. Allow to cool and make up to 200 ml. with cold water.

Determination of Fe_2O_3. Take 100 ml. of the solution of mixed sulphates, add 20 ml. of sulphurous acid, and boil until the excess is driven off. Add 10 ml. of 1 : 1 sulphuric acid and titrate with N/10 solution of potassium dichromate, using potassium ferricyanide as external indicator. The solution is titrated until a spot gives no blue coloration with the indicator.

$$\text{ml. N/10 } K_2Cr_2O_7 \text{ used} \times 1{\cdot}6 = \text{percentage of } Fe_2O_3$$

Solutions required:

(1) N/10 $K_2Cr_2O_7 = 4{\cdot}903$ gram/litre
(2) Potassium ferricyanide $= 0{\cdot}5$ gram/litre.

Solution (2) should be prepared for use on the same day and should not be stored.

Determination of TiO_2. Take 40 ml. of the 200-ml. solution of mixed sulphates in a 50-ml. Nessler tube. Add 6 ml. of 1 : 1 sulphuric acid and 4 ml. of hydrogen peroxide. A yellow colour will be produced if titanium is present. To a similar tube add 40 ml. of a 4-per-cent solution of potassium sulphate, 6 ml. 1 : 1 sulphuric acid and 4 ml. of hydrogen peroxide. Titrate this solution with a standard solution of titanium oxide until the colour matches that of the first tube. Keep the bulk of the solutions equal by making up the first tube with cold distilled water.

$$\frac{\text{ml. of } TiO_2 \text{ solution used}}{2} = \text{percentage of } TiO_2$$

Standard solution of TiO_2:

Heat 3·0 gram of pure, recrystallized potassium fluorotitanate, K_2TiF_6, with sulphuric acid in a platinum dish until all the fluorine is evolved. Add a little more sulphuric acid and evaporate to small volume, but not to dryness. Repeat the treatment several times. Finally dilute with 5-per-cent sulphuric acid to 1 litre.

Preserve the solution in a glass-stoppered bottle with the stopper coated with vaseline. Always withdraw the solution by means of a pipette—never by pouring it out.

Alumina, Al_2O_3, is determined by difference, subtracting the sum of the iron and titanium oxides from the total percentage of mixed oxides.

Lime. Boil the filtrate from the mixed oxide precipitation until the bulk is convenient to handle. Remove from the hot plate and add carefully 2 to 3 gram of ammonium oxalate crystals. Boil for 2 minutes and filter. Wash with hot water through a No. 4 Whatman filter paper; ignite the paper and precipitate in a tared crucible at 1000° C. Cool and weigh as CaO.

Magnesia. Take the filtrate from the lime estimation. Add 40 ml. of 1 : 1 ammonium hydroxide and 20 ml. of a saturated solution of microcosmic salt. Stir well with a glass rod for 3 to 4 minutes, and allow to stand for 1 hour. Filter and wash with a 2½-per-cent solution of ammonium hydroxide. Dissolve the precipitate in hot 1 : 1 hydrochloric acid, using not more than 30 ml. of dilute acid. Wash the paper with hot distilled water and dilute to 200 ml. Add 20 ml. of saturated microcosmic salt solution and allow to settle for ½ hour. Filter, wash with 2½-per-cent ammonium hydroxide solution and dry. Ignite very slowly to 800° C. Cool and weigh.

$$\text{Weight of residue} \times 36{\cdot}2 = \text{percentage of MgO}$$

Alkalies. The ash is heated with a mixture of ammonium chloride and calcium carbonate. By this means the alkalies are obtained in the form of chlorides, while the remaining metals are for the most part left behind as oxides, silicates and aluminates. The silica is changed to calcium silicate.

The changes are represented by the following equations:

$$CaCO_3 + 2NH_4Cl = CaCl_2 + 2NH_4OH + CO_2$$

$$2KAlSi_3O_8 + CaCl_2 + 6CaCO_3 = 6CaSiO_3 + Ca(AlO_2)_2 + 2KCl + 6CO_2$$

The alkali chlorides, together with the excess of calcium chloride, can be removed from the sintered mass by leaching with water, while the other constituents remain undissolved. It is necessary to use the purest reagents possible and a blank should be carried out on the ammonium chloride and calcium carbonate and the appropriate amount of alkali deducted from the quantity found.

Procedure—Weigh 1 gram of ash and mix thoroughly with an equal part of ammonium chloride in a platinum crucible. Add 6 gram of calcium carbonate (free from alkalies). Mix and cover with 2 gram of calcium carbonate. Heat the covered crucible very gently, so that the ammonium chloride does not escape. Raise the temperature slowly until the lower third of the crucible is at a good red heat. Maintain this temperature for 15 minutes. Cool and transfer the sintered mass to a porcelain dish. Wash out the crucible with water into the dish and add more water until the volume is 200–300 ml. Digest at 100° C., breaking lumps with a glass rod, then boil for 5 to 10 minutes. Add ammonium carbonate solution and allow to stand for 20 to 30 minutes.

Filter into a porcelain dish and wash thoroughly with hot water containing ammonium carbonate. Evaporate nearly to dryness; add ammonium hydroxide and ammonium oxalate solutions. Filter into a platinum dish. Evaporate to dryness and ignite gently to drive off ammonium salts. Cool, add ammonium carbonate and ammonium oxalate solution. Filter through a very small filter into a weighed platinum dish. Evaporate to dryness and ignite gently until all the ammonium salts are volatilized. Raise the temperature until the bottom of the dish is a faint red colour: cool and moisten with a drop or two of concentrated hydrochloric acid. Heat again and weigh as the mixed chlorides of sodium and potassium.

Dissolve the alkali chlorides in hot water and transfer to a beaker. Titrate with standard silver solution, containing 10 gram/litre, using potassium chromate as indicator.

Percentage of Na_2O = (ml. $AgNO_3$ × 0·855)
— (weight of mixed chlorides × 195).

Percentage of K_2O = (weight of mixed chlorides × 291)
— ml. $AgNO_3$.

PART V

GENERAL CHEMICAL AND MATHEMATICAL DATA

TABLE OF INTERNATIONAL ATOMIC WEIGHTS*

O=16·00

Aluminium	Al	27·1
Antimony	Sb	121·76
Argon	A	39·94
Arsenic	As	74·96
Barium	Ba	137·37
Bismuth	Bi	209·00
Boron	B	10·82
Bromine	Br	79·92
Cadmium	Cd	112·40
Caesium	Cs	132·91
Calcium	Ca	40·07
Carbon	C	12·00
Cerium	Ce	140·13
Chlorine	Cl	35·46
Chromium	Cr	52·00
Cobalt	Co	58·97
Columbium	Cb	92·91
Copper	Cu	63·57
Dysprosium	Dy	162·46
Erbium	Er	167·2
Europium	Eu	152·0
Fluorine	F	19·0
Gadolinium	Gd	156·9
Gallium	Ga	69·72
Germanium	Ge	72·5
Glucinum (Beryllium)	Gl	9·02
Gold	Au	197·2
Hafnium	Hf	178·6
Helium	He	4·00
Holmium	Ho	164·94
Hydrogen	H	1·008
Indium	In	114·8

* Based upon J.A.C.S., 1943.

Iodine	I	126·92
Iridium	Ir	193·1
Iron	Fe	55·84
Krypton	Kr	83·7
Lanthanum	La	138·92
Lead	Pb	207·21
Lithium	Li	6·94
Lutecium	Lu	174·99
Magnesium	Mg	24·32
Manganese	Mn	54·93
Mercury	Hg	200·6
Molybdenum	Mo	96·0
Neodymium	Nd	144·3
Neon	Ne	20·2
Nickel	Ni	58·68
Niton (Radon)	Nt	222·0
Nitrogen	N	14·01
Osmium	Os	190·2
Oxygen	O	16·00
Palladium	Pd	106·7
Phosphorus	P	30·98
Platinum	Pt	195·23
Potassium	K	39·10
Praseodymium	Pr	140·92
Radium	Ra	226·05
Rhenium	Re	186·31
Rhodium	Rh	102·9
Rubidium	Rb	85·45
Ruthenium	Ru	101·7
Samarium	Sm	150·4
Scandium	Sc	45·1
Selenium	Se	78·96
Silicon	Si	28·06
Silver	Ag	107·88
Sodium	Na	23·00
Strontium	Sr	87·63
Sulphur	S	32·07
Tantalum	Ta	180·88
Tellurium	Te	127·61
Terbium	Tb	159·2
Thallium	Tl	204·39
Thorium	Th	232·12
Thulium	Tm	169·4

Tin	Sn	118·7
Titanium	Ti	47·9
Tungsten	W	183·92
Uranium	U	238·07
Vanadium	V	50·95
Xenon	Xe	131·3
Ytterbium	Yb	173·04
Yttrium	Y	88·92
Zinc	Zn	65·37
Zirconium	Zr	91·22

FACTORS FOR USE IN GRAVIMETRIC ASSAYING

Found	*Sought*	*Factor*
$AlPO_4$	Al_2O_3	0·4178
”	Al	0·2211
Am.Phos	P	0·0163
Molybdate	P_2O_5	0·0373
$BaSO_4$	Ba	0·5885
”	BaO	0·6570
”	S	0·1373
”	SO_3	0·3430
Bi_2O_3	Bi	0·8946
BiOCl	”	0·8024
$CaSO_4$	CaO	0·4119
$CdSO_4$	Cd	0·5392
”	CdO	0·6154
Co_3O_4	Co	0·7343
Cr_2O_3	Cr	0·6842
Fe_2O_3	Fe	0·6994
$Mg_2P_2O_7$	Mg	0·2184
”	MgO	0·3621
Mn_3O_4	Mn	0·7203
Ni-Glyox	Ni	0·2032
$PbSO_4$	Pb	0·6832
”	PbO	0·7360
$PbMoO_4$	Pb	0·5643
”	PbO	0·6078
SiO_2	Si	0·4672
SnO_2	Sn	0·7877
TiO_2	Ti	0·6005
WO_3	W	0·7931
$Zn_2P_2O_7$	Zn	0·4289
Al_2O_3	Al	0·5291

COEFFICIENTS OF DECINORMAL SOLUTIONS

Potassium Permanganate

	gram
Fe	0·00558
Sb	0·00601
Ca	0·00200
CaO	0·00280
Cd	0·00140
CdO	0·00160
Cr	0·00173
Cr_2O_3	0·00253
Ti	0·00481
U	0·01191
V	0·00510

Potassium Bichromate

	gram
Fe	0·00558
FeO	0·00718
Fe_2O_3	0·00798
Cr	0·00173
Cr_2O_3	0·00253
Mn	0·00275
MnO	0·00355
MnO_2	0·00435

Iodine

	gram
As	0·00375
As_2O_3	0·00495
Cd	0·00562
CdS	0·00642
SO_2	0·00320
Sn	0·00594

Sodium Thiosulphate

	gram
Cu	0·006357
Pb	0·006900
PbO	0·007433
S	0·001067
Ba	0·004577

Silver Nitrate

	gram
Cl	0·003546
NaCl	0·005846

Ammon. Potass. Thiocyanate

	gram
Ag	0·010790
Cl	0·003546

STANDARD SOLUTIONS USED IN VOLUMETRIC ASSAYING

Note. It is essential that all solutions are standardized in every case under exactly the same conditions as obtain in the assay of the sample.

		grams per litre
Potassium permanganate	N/10	3·156
Potassium bichromate	„	4·193 (8·8)
Iodine	„	12·7 (18 gram KI)
Sodium thiosulphate	„	24·8 (40·0)
Silver nitrate	„	16·966
Potassium thiocyanate	„	10·0
Ammonia	„	9·0
Potassium ferrocyanide	„	14·4 (43·0)
Ammonium molybdate	„	9·32
Uranium acetate	„	25·5

In most laboratories it is the usual procedure to employ solutions so adjusted that 1 ml. is equivalent to 10 mg. of the metal to be estimated, so that where 1 gram is taken for a trial, 1 ml. on the burette is equivalent to 1 per cent. An example is given below of the calculation necessary to find the weight of material necessary to dissolve in a litre of water, where the quantities per litre of the decinormal solution are known.

To obtain a 10-mg. solution of sodium thiosulphate:

1 ml. N/10 solution=0·006357 gram Cu.
0·006357 gram Cu : 24·8 : : 0·010 gram Cu : x

A 10-mg. solution of " hypo " contains 40 gram per litre (approx.). These solutions are commonly prepared as 10 mg., so the quantities of salt per litre for such are given in brackets at the side. It will be seen that a decinormal solution is only decinormal for the purpose for which it has been prepared; for instance, N/10 " hypo " is equivalent to 0·006357 gram of Cu per millilitre, but when used for lead it is equivalent to 0·0069 gram of lead per millilitre, since one atom of Pb as chromate is equivalent to three atoms of iodine, and not two, according to its normal valency.

MISCELLANEOUS REAGENTS FOR VOLUMETRIC ASSAYING

Standard ferrous sulphate solution:

A.R. ferrous ammonium sulphate	84 gram
A.R. sulphuric acid	200 ml.
Distilled water	to 1 litre

1 ml. equals about 12 mg. of Fe

" Tambon " solution:

Distilled water	250 ml.
A.R. ammonia 0·880 s.g.	150 ml.
A.R. ammonium chloride	70 gram

Acidulated salt solution (for lead):

Pure salt	550 gram
A.R. hydrochloric acid	250 ml.
Distilled water	2,000 ml.

Paper pulp:

Tear up some filter papers (No. 4 Whatman are the best) into small pieces, and insert into a litre flask by means of a glass rod. Add a few millilitres of hot water and shake well until the pulp collects in a ball, adding further quantities of water as required. Fill flask from the tap with cold water, shake well, and the pulp is ready to use. To use in a funnel, inset the latter in a rubber stopper which fits tightly in the neck of the pressure flask. Lay a filter disc at the bottom of the funnel, hold it in position with the tip of a glass rod, and pour the pulp over it to a height of about an inch and a half over the disc. Connect up the flask to the tap and draw through the excess water.

REACTIONS INVOLVED IN VOLUMETRIC ASSAYS

Antimony:

$5Sb_2O_3+4KMnO_4=5Sb_2O_5+2K_2O+4MnO.$

Arsenic:

(1) $As_2O_3+2I_2+2H_2O=As_2O_5+4HI$

(2) $H_2AsO_4+(UO_2)(C_2H_3O_2)_2=(UO_2)AsO_4+2C_2H_4O_2.$

Barium:

$2BaCrO_4+6KI=Cr_2O_3+3K_2O+3I_2$; and

$I_2+2Na_2S_2O_3=Na_2S_4O_6+2NaI.$

Cadmium:

(1) $8KMnO_4+5CdS+24HCl=8KCl +8MnCl_2+5CdSO_4+12H_2O.$

(2) $CdS+2HCl+I_2=CdCl_2+2HI+S.$

Calcium:

$5Ca(COO)_2+2KMnO_4=K_2O+2MnO+10CO_2+5CaO.$

Chromium:

$2CrO_3+6FeO=3Fe_2O_3+Cr_2O_3.$

Copper:

$2CuO+2KI=Cu_2O+K_2O+I_2$; and

$I_2+2Na_2S_2O_3=Na_2S_4O_6+2NaI.$

Iron:

(1) $K_2Cr_2O_7+6FeO=3Fe_2O_3+K_2O+Cr_2O_3.$

(2) $2KMnO_4+10FeO=K_2O+2MnO+5Fe_2O_3.$

Lead:

(1) $(CH_3COO)_2Pb+(NH_4)_2MoO_4=PbMoO_4+2(CH_3COO)NH_4.$

(2) $2PbCrO_3+6KI+HCl=2CrCl_3+6KCl+3I_2+8H_2O.$

$I_2+2Na_2S_2O_3=Na_2S_4O_6+2NaI.$

Manganese:

(1) $MnO(OH)_2+(COOH)_2=MnO+2CO_2+2H_2O$.
(2) $3MnO+2KMnO_4=5MnO_2+K_2O$.

Molybdenum, see Lead.

Silver:

(1) $AgNO_3+KCNS=KNO_3+AgCNS$.
(2) $AgK(CN)_2+I_2=KI+ICN$ and $AgCN+I_2=AgI+ICN$.

Sulphur, see Barium.

Tin:

$SnCl_2+2HCl+I_2=SnCl_4+2HI$.

Uranium:

$$5U(SO_4)_2+2KMnO_4+2H_2O=5(UO_2)SO_4+2MnSO_4+2KHSO_4+H_2SO_4.$$

Vanadium:

$5V_2O_4+2KMnO_4=5V_2O_5+K_2O+2MnO$.

Zinc:

$K_4Fe(CN)_6+2ZnCl_2=Zn_2Fe(CN)_6+4KCl$; and
$3Zn_2Fe(CN)_6+K_4Fe(CN)_6=2K_2Zn_3(Fe(CN)_6)_2$.

Metallic Zn in Zn dust:

(1) $Zn+CuSO_4=ZnSO_4+Cu$.
(2) $Fe_2O_3+H_2=2FeO+H_2O$.

MnO_2 in Mn ores:

(1) $MnO_2+2FeO=MnO+Fe_2O_3$.
(2) $MnO_2+4HCl+2KI=MnCl_2+2H_2O+2KCl+I_2$; and
$I_2+2Na_2S_2O_3=Na_2S_4O_6+2NaI$.

USEFUL DATA

BRITISH WEIGHTS AND MEASURES AND THEIR METRIC EQUIVALENTS

LONG MEASURE

British	*Metric*	*Reciprocal*
1 inch	2·5400 cm.	0·3937
1 foot	0·3040 m.	3·2808
1 yard	0·9144 m.	1·0936
1 mile	1·6093 km.	0·6214

SQUARE MEASURE

British	*Metric*	*Reciprocal*
1 sq. in.	6·453 sq. c.	0·1550
1 sq. ft.	0·0929 sq. m.	10·7639
1 sq. yd.	0·836 sq. m.	1·1960

CUBIC MEASURE

1 cu. in.	16·387 c.c.	0·061
1 cu. ft.	0·028 c.m.	35·315
1 cu. yd.	0·7646 c.m.	1·308

CAPACITY

1 oz.	28·35 c.c.	0·0353
1 pint	0·5681 litre	1·760
1 gallon	4·546 litre	0·220

WEIGHT (AVOIR.)

1 dram	1·772 gram	0·5644
1 ounce	28·350 gram	0·0353
1 lb.	0·4536 kilo	2·2046
1 cwt.	50·8020 kilo	0·0197
1 ton	1·016 tonne	0·9842

CONVERSION TABLES:
DEGREES CENTIGRADE INTO DEGREES FAHRENHEIT

C tens	0	1	2	3	4	5	6	7	8	9
0	32·0	33·8	35·6	37·4	39·2	41·0	42·8	44·6	46·4	48·2
10	50·0	51·8	53·6	55·4	57·2	59·0	60·8	62·6	64·4	66·2
20	68·0	69·8	71·6	73·4	75·2	77·0	78·8	80·6	82·4	84·2
30	86·0	87·8	89·6	91·4	93·2	95·0	96·8	98·6	100·4	102·2
40	104·0	105·8	107·6	109·4	111·2	113·0	114·8	116·6	118·4	120·2
50	122·0	123·8	125·6	127·4	129·2	131·0	132·8	134·6	136·4	138·2
60	140·0	141·8	143·6	145·4	147·2	149·0	150·8	152·6	154·4	156·2
70	158·0	159·8	161·6	163·4	165·2	167·0	168·8	170·6	172·4	174·2
80	176·0	177·8	179·6	181·4	183·2	185·0	186·8	188·6	190·4	192·2
90	194·0	195·8	197·6	199·4	201·2	203·0	204·8	206·6	208·4	210·2
100	212·0	213·8	215·6	217·4	219·2	221·0	222·8	224·6	226·4	228·2

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GENERAL QUALITATIVE ANALYSIS SCHEME FOR METALS

MAKE SOLUTION OF COMPOUND IN WATER OR DILUTE NITRIC ACID

Add hydrochloric acid

<table>
<tr>
<td colspan="3">Precipitate
Hg(ous) Pb Ag
Wash, boil with water, filter hot</td>
<td colspan="21">Filtrate
Cd Cu Hg(ic) Pb Bi As(ous)(ic) Sb Sn(ous)(ic) Zn Mn Co Ni Al Fe(ous)(ic) Cr Ba Sr Ca Mg Li K Na NH_4
Pass H_2S through the liquid, filter</td>
</tr>
<tr>
<td colspan="2">Residue
Hg(ous) Ag
Wash, add NH_4OH</td>
<td rowspan="5">Filtrate
Pb
Add
H_2SO_4
White
ppt.</td>
<td colspan="8">Precipitate
Cd Cu Hg(ic) Pb Bi As Sb Sn
Collect, wash, digest with NH_4HS and S, filter</td>
<td colspan="13">Filtrate
Zn Mn Co Ni Al Fe Cr Ba Sr Ca Mg Li K Na NH_4
Add NH_4Cl, NH_4OH and NH_4HS, warm gently, and filter</td>
</tr>
<tr>
<td rowspan="4">Res.
Hg(ous)
Black</td>
<td rowspan="4">Filtrate
Ag
Add
HNO_3
White
ppt.</td>
<td colspan="5">Precipitate
Cd Cu Hg(ic) Pb Bi
Wash, boil in HNO_3, filter</td>
<td colspan="3">Filtrate
As Sb Sn
Add dilute HCl, filter, drain well, add concentrated HCl, boil, dilute slightly, filter</td>
<td colspan="6">Precipitate
Zn Mn Co Ni Al Fe Cr
Collect, wash, dissolve in HCl, with a few drops of HNO_3, boil, add NH_4OH, stir, filter</td>
<td colspan="7">Filtrate
Ba Sr Ca Mg Li K Na NH_4
Add $(NH_4)_2CO_3$, warm, filter</td>
</tr>
<tr>
<td rowspan="3">Residue
Hg(ic)
Black
Confirm
by Cu strip
test in
original
solution
cf.
page 19</td>
<td colspan="4">Filtrate
Cd Cu Pb Bi
Add NH_4OH, filter</td>
<td rowspan="3">Residue
As
Yellow
Confirm by
Fleitmann's
test
cf.
page 36</td>
<td colspan="2">Filtrate
Sn Sb
Pour into H-apparatus</td>
<td colspan="3">Precipitate
Fe Al Cr
Wash, dry, fuse on Pt foil with Na_2CO_3 and KNO_3, boil in water, and filter</td>
<td colspan="3">Filtrate
Zn Mn Co Ni
Acidify with acetic acid, pass H_2S, filter</td>
<td colspan="3">Precipitate
Ba Sr Ca
Collect, wash, dissolve in acetic acid, add excess of K_2CrO_4, filter</td>
<td colspan="4">Filtrate
Mg K Na NH_4
Add $(NH_4)_2HPO_4$, warm, stir, filter</td>
</tr>
<tr>
<td colspan="2">Precipitate Pb Bi
Wash, add a few drops HNO_3, dilute, filter</td>
<td colspan="2">Filtrate
Cd Cu
Add KCN and H_2S</td>
<td rowspan="2">Sn
remains on
Zn
Dissolve in
HCl, and
apply tests
on
page 41</td>
<td rowspan="2">Sb
escapes as
SbH_3
Test as
usual
for stain on
porcelain
lid
cf. page 39</td>
<td rowspan="2">Residue
Fe_2O_3
Brown
Test
original
solution
for
ferrous
or ferric
state
cf.
pages 47
and 48</td>
<td colspan="2">Filtrate
If yellow, Cr present
Divide into two parts</td>
<td rowspan="2">Sol.
Mn add
NH_4OH
and
NH_4HS
Buff,
turning
brown.
Search
also for
Mn in the
Fe Al Cr
ppt.</td>
<td colspan="2">Precipitate
Zn Co Ni
Boil with HCl and a little HNO_3; add KOH, filter</td>
<td rowspan="2">Ppt.
Ba
Yellow</td>
<td colspan="2">Filtrate
Sr Ca
Add dilute H_2SO_4, let stand, filter</td>
<td rowspan="2">Ppt.
Mg
White</td>
<td colspan="3">Filtrate
K Na NH_4
Evaporate to small bulk, and filter</td>
</tr>
<tr>
<td>Ppt.
Bi
White
ppt.</td>
<td>Filt.
Pb
Add
H_2SO_4,
set aside;
white
ppt.</td>
<td>Ppt.
Cd
Yellow.</td>
<td>Filt.
Cu
Acidify
with
acetic
acid
Brown
ppt.</td>
<td>Sol.
Al
Add
excess
of
NH_4Cl
and
boil off
NH_3
White
ppt.</td>
<td>Sol.
Cr
Add
acetic acid
and
excess of
$AgNO_3$
Red ppt.
Or boil with
H_2SO_4 and
alcohol
Green sol.</td>
<td>Filtrate
Zn.
Add
NH_4HS
White
ppt.</td>
<td>Precipitate
Co Ni
Dissolve in
HCl and test
by borax bead
cf. page 6</td>
<td>Ppt.
Sr
White</td>
<td>Filtrate
Ca
Add NH_4OH
and
ammoniun
oxalate
White ppt.</td>
<td></td>
<td></td>
<td>Filtrate
K Na NH_4
Evaporate,
ignite,
dissolve.
Test for K by
H_2PtCl_6
(page 87)
Na by flame
NH_4 in original
solution</td>
</tr>
<tr>
<td colspan="3">Group I</td>
<td colspan="5">Group IIA</td>
<td colspan="3">Group II B</td>
<td colspan="3">Group III</td>
<td colspan="3">Group IV</td>
<td colspan="3">Group V</td>
<td colspan="4">Group VI</td>
</tr>
</table>